STUDIES ON INHIBITION OF METALLIC CORROSION

THESIS

SUBMITTED FOR THE AWARD OF THE DEGREE OF

Doctor of Philosophy

IN

APPLIED CHEMISTRY

BY

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Summary

Corrosion is a major problem in several industries. It causes enormous wastage of metallic materials, which leads to heavy economic losses all over the world. In India the monetory losses due to corrosion have been established as high as Rs. 30,000 crores per year.

Among the available methods of preventing corrosion, the use of inhibitors is one of the most promising methods particularly for closed systems. Due to the ease of application and cost-effectiveness, it has attracted a great deal of attention of corrosion scientists and engineers all over the world.

Million of rupees worth metals and alloys are lost every year due to atmospheric corrosion, results from individual and combined action of oxygen, moisture and atmospheric pollutants.

There are several ways to prevent atmospheric corrosion. The use of vapour phase corrosion inhibitors (VCIs) is an effective and relatively inexpensive method of controlling corrosion problem in closed environment. VCIs control corrosion of metals and alloys even in the presence of high humidity, temperature and atmospheric pollutants such as SO_2, H_2S and even chlorine, VCIs having an appropriate vapour pressure possess high passivating properties, strong tendencies towards surface adsorption and the ability to form a strong and stable bond with the metal surface.

Process industries require enormous amount of water to provide heat reduction at various stages of manufacturing process. This heat reduction is carried out in cooling water system. Treating the cooling water system with inhibitors reduce the aggressiveness of the environment towards metal. The role of cooling water inhibitors in industries is to permit more extensive use of iron and carbon or low alloy steel and brass as components by protectcing them from corrosive medium.

The research work embodied in the present thesis deals with study of corrosion inhibition of metals and alloys in vapor phase conditions and the study of corrosion inhibition in cooling water systems. The techniques such as weight loss method, Eschke test, salt inoculation test, SO_2 test, potentiodynamic polarization method,

Knudsen method for vapour pressure determination and auger electron spectroscopy have been used in corrosion inhibition study.

The thesis comprises of three chapters. The first chapter presents introduction , which highlights the economic and technological importance of corrosion. Theories of corrosion have also been described, which help in understanding the mechanism of corrosion. Special attention has been given to explain the mode of action of inhibitors towards corrosion control. The account of various techniques used for investigating corrosion inhibitors has been discussed briefly. A survey of the literature on vapour phase corrosion inhibitors and cooling water inhibitors has been given. The aims and objectives have also been mentioned.

The description of inhibitor synthesis and details of experimental techniques such as weight loss method, Eschke test, salt inoculation test, SO_2 test, potentiodynamic polarization method; Knudsen method for vapour pressure determination ,auger electron spectroscopy for best performed VCI and atomic absorption spectroscopy for solution analysis used are given in the chapter second.

The third chapter describes discussion of results obtained from these studies. The compounds examined in the present investigation are given in Table 1. Their inhibiting action has been discussed separately in the following two parts:

Part A: Corrosion inhibition by vapour phase corrosion inhibitors (VCIs)

- Section -1 Hydrazide and its salts as VCIs
- Section –2 Schiff's bases as VCIs
- Section –3 Imidazoline salts as VCIs

Part B: Corrosion inhibition by cooling water inhibitors

- Section-1 Triazole derivatives as corrosion inhibitors for brass
- Section-2 Natural compounds as cooling water inhibitors for mild steel

The results of the present investigations revealed the fact that hydrazide and its salts inhibit the corrosion of ferrous and non-ferrous metals under vapour phase condition. The order of inhibition efficiency has been found as follows:

LHC > LHNB > LHP > LHM > LHS >LH

BHB > BHS > BHN > BH

The higher inhibition efficiency of LHC may be attributed to the presence of an additional π bond between carbon atoms of cinnamate onto the metal surface. BHB showed good inhibition efficiency due to the presence of extensively delocalized π electrons in benzene ring further facilitates the adsorption process.

The inhibition of corrosion by Schiff's bases may be explain on the basis of the presence of π electrons of benzene ring and azomethine group (-C=N-), which facilitates adsorption of molecules onto metal surface. CLH exhibited the better performance than SLH due to presence of additional π bond between carbon atoms (-C=C-), conjugated to azomethine group (-C=N-).BBH showed good inhibition efficiency due to the presence of extensively delocalized π electrons in benzene ring further facilitates the adsorption process. The lower inhibition efficiency of SBH, CBH, may be attributed to the orientation of the substituent group,which prevents aflat orientation on the metal surface causing less adsorption. The order of inhibition efficiency of schiff's bases as follows:

CLH > SLH

BBH >SBH >CBH

The order of inhibition efficiency of 1-(2-amino ethyl)-2-dec-9 enyl-2 imidazoline salts and 1-(2-amino ethyl)-2-undecyl-2 imidazoline salts have been found as follows:

ADIC >ADIP >ADIN > ADIS

AUIC >AUIP >AUIN > AUIM

The corrosion inhibiting action of the imidazoline salts is attributed to the presence of lone pair of electrons present on the N atoms of the inhibitor molecules, which facilitate adsorption onto metal surface. Cinnamate salts of imidazoline exhibited highest inhibition efficiency for ferrous and non-ferrous metals may be attributed to the presence of an additional π bond between carbon atoms(-C=C-) which further facilitate greater adsorption onto metal surface.

The triazole derivatives were found to inhibit corrosion of brass in NaCl water solution. The inhibition efficiencies increased with increase in triazole derivatives

concentration until the maximum efficiency was obtained at an optimum concentration 300 ppm. The ranking of inbition efficiencies was as follows:

ABMT > AHMT

The inhibition of brass suface might have occurred due to complex formation of copper with triazoles.

The extract of natural products inhibits corrosion of mild steel in NaCl water solution. The inhibition efficiency of examined extracts increases with inhibitor concentration until the maximum efficiency was obtained at an optimum concentration .The order of inhibition efficiency of the exracts was follows as :

AS > AP >OB

The corrosion inhibiting action of aqueous exract of natural products is attributed to the presence of sulphur, nitrogen, and oxygen containing organic compounds.

The results from Eschke test, salt inoculation test and SO_2 test showed inhibition of corrosion of different metals by VCIs.

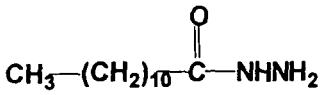
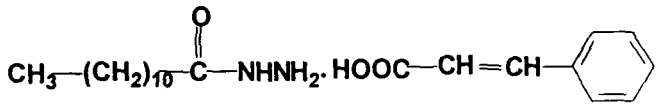
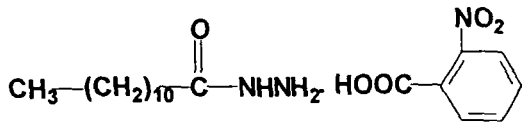
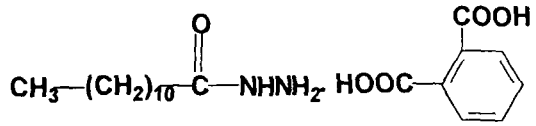
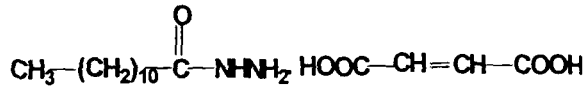
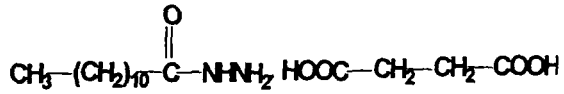
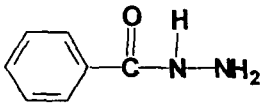
The vapour pressure of all the compounds(VCIs) was determined by using knudsen method. All the organic compounds were found effective.

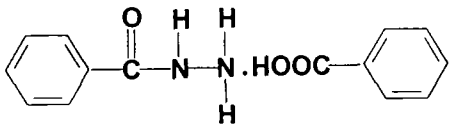
The potentiodynamic polarization studies were carried out at room temperature. The polarization behaviour of different series of vapour phase corrosion inhibitors and cooling water inhibitors was studied. All the vapour phase corrosion inhibitors were found to be anodic type inhibitors. The compounds used as cooling water inhibitors were found to be mixed type inhibitors.

The atomic absorption specrtrophotometer used to analyse the concentation of zinc and copper in ppm. The lowest concentration of zinc achieved in solution with the optimum inhibitors concentration.

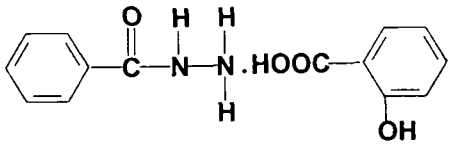
The best performed VCI was studied by the technique auger electron spectroscopy which showed the adsorption of chemical species of the inhibitor on metal surface.

Table 1.0 Name and structures of the compounds studied

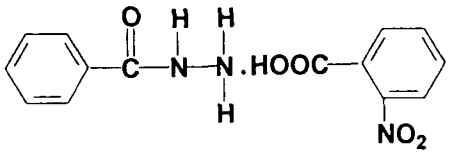
S.No.	Structure	Name and Abbreviation
1.		Lauric hydrazide (LH)
2.		Lauric hydrazide cinnamate (LHC)
3.		Lauric hydrazide nitrobenzoate (LHN)
4.		Lauric hydrazide phthalate (LHP)
5.		Lauric hydrazide maleate (LHM)
6.		Lauric hydrazide succinate (LHS)
7.		Benzoic hydrazide (BH)

8. 

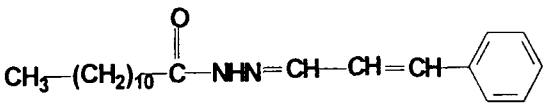
Benzoic hydrazide benzoate (BHB)

9. 

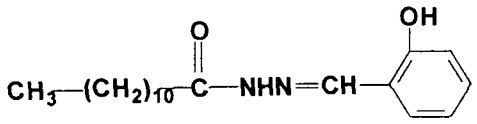
Benzoic hydrazide salicylate (BHS)

10. 

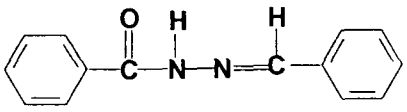
Benzoic hydrazide nitrobenzoate (BHN)

11. 

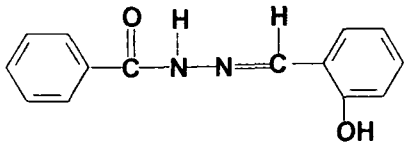
Cinnamylidene lauric hydrazide (CLH)

12. 

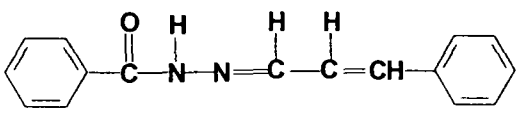
Salicylidene lauric hydrazide (SLH)

13 

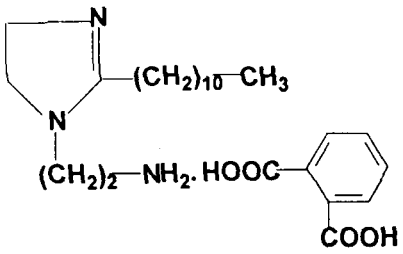
Benzalidene bezoic hydrazide (BBH)

14. 

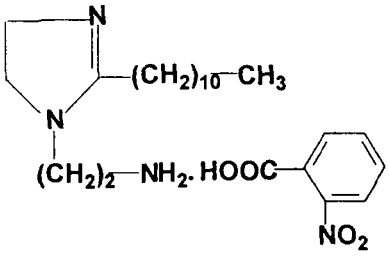
Salicylidene benzoic hydrazide (SBH)

15. 

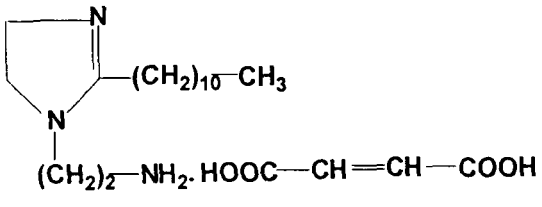
Cinamalidene benzoic hydrazide (CBH)

21. 

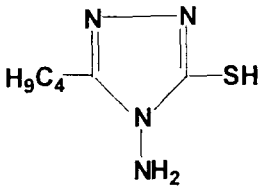
1-(2-aminoethyl)-2 undecyl-2 imidazoline phthalate (AUIP)

22. 

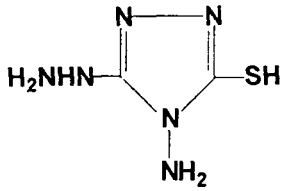
1-(2-aminoethyl)-2 undecyl-2 imidazoline nitrobenzoate (AUIN)

23. 

1-(2-aminoethyl)-2 undecyl-2 imidazoline maleate (AUIM)

24. 

4-Amino-3 butyl-5-mercapto-1,2,4 triazole (ABMT)

25. 

4-Amino-3 hydrazino-5-mercapto- 1,2,4 triazole (AHMT)

26.	Alliin, Allicin(diallylthiosulphide), diallyldisulphide	Allium Sativum (garllic) (AS)
27.	Allyl propyl disulphide, Flavonides such as quercetin	Allium cepa (onion) (AC)
28.	Caffeic acid, tannins, beta carostenes	Ocimum basilcum (tulsi) (OB)

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Dedicated to my Late Father

DEPARTMENT OF APPLIED CHEMISTRY

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CERTIFICATE

This is to certify that the work incorporated in this thesis entitled **"Studies on Inhibition of Metallic Corrosion"** is the original contribution of **Mr. Vikas Bhardwaj** and is suitable for the award of Ph. D degree.

Dr. Ali Mohammad 18/12/07
(Supervisor & Chairman)

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I express my gratitude to my supervisor and chairman, Dr. Ali Mohammad, Department of Applied Chemistry, for his highly support, scholarly guidance and magnanimous attitude.

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Thanks are due to my colleagues, friends and well-wishers for the cooperation they rendered.

I am profoundly grateful to my mother, elder brother Mr. Vivek Bhardwaj and sisters- Ms. Alka Bhardwaj and Ms. Anamika Bhardwaj, for their affection, encouragement and forever support.

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Vikas Bhardwaj

Vikas Bhardwaj

Preface

Corrosion manifests itself in multifarious forms in our daily lives. It affects the economy of country and causes severe material science problem. The seriousness of the problem has made the corrosion scientist aware and conscious. Corrosion prevention technology has many options at its disposal for successful corrosion mitigation of materials. One of the very important methods of minimizing corrosion today is the use of inhibitors. Corrosion inhibitors are extensively used in various applications and many plant operations are dependent on their successful operation.

There are several ways to prevent atmospheric corrosion. The use of vapour phase corrosion inhibitors (VCIs) is an effective and relatively inexpensive method of controlling corrosion problem in closed environment.

Treating the cooling water system with inhibitors reduce the aggressiveness of the environment towards metal.

This thesis deals with study of corrosion inhibition of metals and alloys in vapor phase conditions and the study of corrosion inhibition in cooling water systems. It includes an introduction, reflecting the economic significance of corrosion problem. The form and theories have been described to explain its mechanism. Prevention and corrosion-control has also been described, with emphasis on mode of action of inhibitors. A brief description of different techniques employed for investigation of corrosion inhibitors has also been given. The literature on corrosion inhibition studies has been incorporated.

The description of inhibitor synthesis and details of experimental techniques such as weight loss method, Eschke test, salt inoculation test, SO_2 test, potentiodynamic polarization method , Knudsen method for vapour pressure determination ,auger electron spectroscopy for best performed VCI and atomic absorption spectroscopy used for solution analysis are given in the experimental part.

The results obtained from weight loss measurements, Eschke test, SO_2 test, salt inoculation test and potentiodynamic polarization measurements have been discussed in sections in terms of various corrosion parameters such as inhibition efficiency, corrosion rate, corrosion current , corrosion potential and in terms of visual observations. To reveal some more information about the inhibition, best performed inhibitor has been evaluated by auger electron spectroscopy

The research work embodied in the present thesis deals with study of corrosion inhibition of metals and alloys in vapor phase conditions and the study of corrosion inhibition in cooling water systems. The techniques such as weight loss method, Eschke test, salt inoculation test, SO_2 test, potentiodynamic polarization method, Knudsen method for vapour pressure determination, auger electron spectroscopy and atomic absorption spectroscopy for solution analysis have been used in corrosion inhibition study. The atomic absorption specrtroscopy has been used to analyse the concentration of zinc and copper. The mechanism of corrosion inhibition has also been discussed.

CONTENTS

Chapter-1

Introduction

Corrosion can be defined in many ways. The one more preferred in literature is the degradation of useful properties of material as a result of chemical or electrochemical reaction with its environment (1). Degradation due to purely mechanical forces is not called corrosion but is known as wear, fretting etc. In some cases chemical or electrochemical attack may be accompanied by physical deterioration and is described by terms corrosion–erosion, corrosion-wear or fretting corrosion.

The well-recognized example of metallic corrosion is the rusting of iron and steel. Beside this there are numerous other familiar examples of corrosion reactions. Silver articles tarnish and finally go black in the atmosphere; the transformation of silver to its black sulphide does not amount to a serious loss of the costly metal, but steps have to be taken to restore the surface to its former luster. A similar loss of appearance is involved in the dulling of brass and fogging of nickel.

Trends in corrosion research had changed rapidly over the years. In fifties, polarization studies and their applications had been the topic of interest (2,3). In the seventies corrosion research was concentrated on the mechanistic studies on metal dissolution, localized corrosion and high temperature corrosion (4-7). In recent years corrosion research has been diversified into several newer fields. Optical techniques have revolutionized the field. Surface analytical techniques play a major role since; they give more insight into the understanding of the nature and the influence of surface of surface oxides on the corrosion of metals and alloy. These techniques are helpful to characterize the thickness, the structure and the composition of films. Computers (8) and microprocessors (9) find application in analyzing the corrosion data.

Corrosion engineering is the science and art to prevent or control corrosion economically and safely. The ultimate objective of all electrochemists, metallurgists and chemical engineers is to understand the mechanism of corrosion and minimize corrosion failures.

1.1 ECONOMIC IMPORTANCE OF CORROSION

Corrosion poses a very serious problem to industries affecting both to the cost and the productivity. Loses due to corrosion are so high that it has assumed great economic importance throughout the world. It is expected that 25% of the total product of the metal and alloys go waste due to corrosion. The losses due to corrosion, which were modest when process and material were simple, grew exponentially, to the astronomic figures of over Rs. 6,40,000 million per year by 1977, amounting for losses equal to about one percent of the gross world product (10).

Even in the industrially developed countries like USA and UK, corrosion is posing very serious problems, which can be appreciated by the fact that Canada is spending $1 billion annually to control corrosion, while in UK the total loss due to corrosion is of the order of £600 million (11). According to NACE (International) bulletin (12) the annual losses due to corrosion in USA were estimated to be more than $300 billion. In India the annual losses due to corrosion has increased to more than Rs.25,000 crores per year.

Thus from economic point of view, it is necessary for corrosion specialists to study corrosion mechanism and various ways and means to minimize corrosion damage.

1.2 FACTORS INFLUENCE CORROSION

The nature and the extent of corrosion depend largely on the metal and environment. Thus factors like structural features of the metal, nature of the environment and the type of reactions that occur at the metal/ environment interface have to be considered for the understanding of the corrosion phenomenon.

The important factors, which influence the corrosion process, are (i) nature of the metal, (ii) nature of the environment, (iii) electrode potential, (iv) temperature, (v) aeration, (vi) agitation, (vii) pH of the solution, (viii) solution concentration, (ix) nature of the corrosion products, and (x) hydrogen over potential

1.3 CLASSIFICATION OF CORROSION

Corrosion has been classified in many different ways as low temperature and high temperature corrosion, direct oxidation and electrochemical corrosion, etc. The preferred classification is (i) Wet or electrochemical corrosion (ii) Dry or chemical corrosion.

i. **Wet or Electrochemical Corrosion** which involves an interface. It can be further separated into:

(a) **Separable anode / cathode type:** In these cases certain areas of the metal can be experimentally identified as predominantly anodic or cathodic. The distances of separation of these areas may be very small, of the order of fractions of millimeter. There is a macroscopic flow of charge through the metal.

(b) **Interfacial anode / cathode type:** In this type one entire interface is cathode and the other is the anode and the charge is transported through a file of reaction product on the metal surface.

(c) **Inseparable anode / cathode type:** Here the anodes and the cathodes cannot be distinguished by experimental methods, though there presence is postulated by theory, e.g. the uniform dissolution of the metal in fused salt non-aqueous solutions, acid, alkaline or neutral solutions.

ii **Dry or Chemical Corrosion** which involves direct chemical reaction of a metal with its environment. There is no transport of electric charge and the metal remain film free. This would include corrosion in gaseous environments when the reaction product is volatile, corrosion in liquid metals, fused halides and organic liquids. A general scheme for the classification of corrosion processes is presented separately in the form of a Table 1.1. Various important form of corrosion with definitions and examples are summarized in Table1.2

Table. 1.1 Classification of corrosion processes

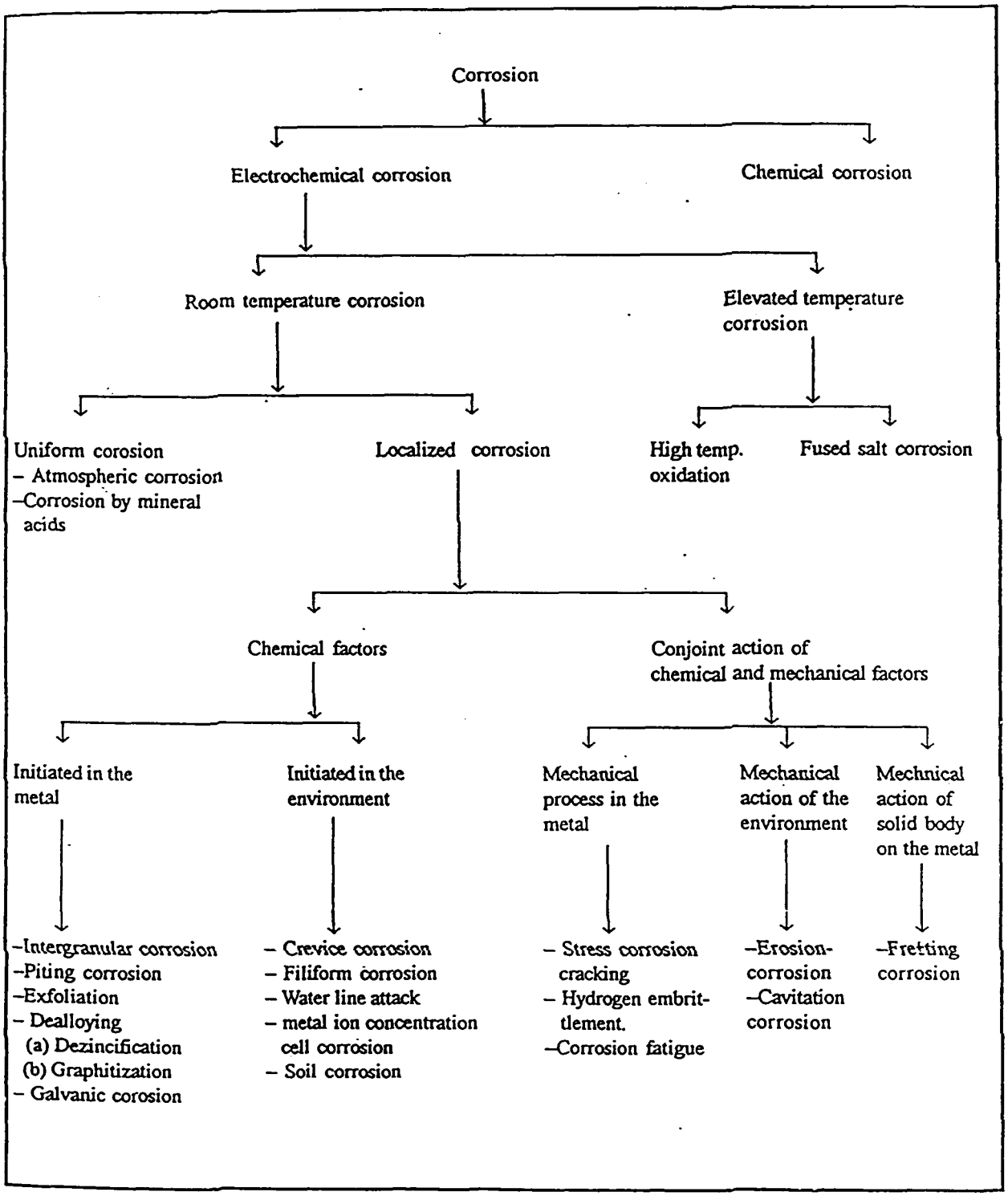


Table 1.2 Various important forms of corrosion with examples

S. No.	Corrosion type	Definition	Examples
1.	Dry corrosion	Involving chemical reaction with non-electrolytic gas or liquid.	Corrosion of steel with SO_2, CO_2, O_2, etc.
2.	Wet corrosion	Corrosion in contacts with electrolyte such as aqueous solution of salt, alkali and acid.	Corrosion of steel in sea water, acids and alkalis.
3.	Uniform corrosion	Uniform attack of electrochemical or chemical reaction over the entire surface.	Steel immersed in dilute sulphuric acid.
4.	Pitting corrosion	Localized attack in the form of pit.	Stainless steel, aluminium alloys, copper alloys, and nickel alloys immersed in chloride solution.
5.	Crevice corrosion	Intense localized corrosion in shallow holes.	The crevices under bold and rivet heads.
6.	Galvanic corrosion	Dissimilar metals immersed in a corrosive media and connected electrically	Zinc and iron in salt solution.
7.	Intergranular corrosion	corrosion occurring in the vicinity of grain boundaries.	Weldments of stainless steel
8.	Stress corrosion cracking	Cracking caused by simultaneous presence of tension stress and particular corrosion medium.	Season cracking of brass and caustic embrittlement of steel.
9.	High temperature oxidation	Oxidation reaction with the products of fuel combustion.	Corrosion of steel with combustion products such as Co_2, SO_2, O_2, etc.
10.	Erosion corrosion	Acceleration of corrosion because of relative movement between corrosive fluid and the metal.	Corrosion in pumping equipment, corrosion in the area between bearings and shafts.
11.	Corrosion fatigue	Combined action of corrosive medium and variable stresses.	Heat exchanger tubes of chemical equipments.

1.4 ELECTROCHEMICAL THEORY OF CORROSION

Most of the corrosion reactions, especially those occurring in aqueous media are electrochemical processes. The overall corrosion process is the contribution of two reactions, the oxidation of metal (anodic process) and an equivalent reduction reaction (cathodic process). An oxidation reaction is indicated by production of electrons as given below :

$$M \rightleftharpoons M^{+} + e^{-} \qquad ---(1)$$

This reaction constitutes the basis of corrosion of metals. In a similar fashion, a reduction reaction is indicated by the consumption of electrons. For every oxidation reaction there must be a corresponding reduction reaction. In aqueous solutions, various reduction reactions are possible depending upon the system. Some examples of reduction reactions are:

Hydrogen evolution: $2H^{+} + 2e^{-} \rightarrow H_2$ (in acidic system) ---(2)

Oxygen reduction: $O_2 + 4H^{+} + 4e^{-} \rightarrow 2H_2O$ (in acidic solution) ---(3)

$O_2 + 2H_2O + 4\,e^{-} \rightarrow 4\,OH^{-}$ (in neutral and alkaline solution) ---(4)

Metal ion reduction: $M^{+n} + e^{-} \rightarrow M^{+(n-1)}$ ---(5)

Metal deposition: $M^{+n} + ne^{-} \rightarrow M$ ---(6)

Oxidation reaction are known as anodic reactions while reduction reactions as cathodic. During the corrosion more than one anodic and cathodic reactions may occur. Oxidation-reduction (redox) reactions can be understood by the example of corrosion of mild steel in sulphiric acid contaminated by ferric ions. Anodic reaction will occurs as follows:

$$M \rightleftharpoons Mn^{+} + ne^{-} \qquad ---(6a)$$

All the components elements of mild steel (e.g. Fe, Mn, etc.) go into the solution as their respective ions. The electrons produced by these anodic (oxidation) reactions will be consumed by the cathodic (reduction) reactions. In this case, reaction (5) can be represented as follows:

$$Fe^{3+} + e^{-} \rightarrow Fe^{2+} \qquad ---(7)$$

Removing one of the available cathodic reactions e.g. reaction (7) by removal of the Fe^{3+} ions will reduce the corrosion rate.

When a metal or alloy is immersed in a corrosive environment (conductive) different potential zones are developed on the surface of metal of alloy due to the presence of different metallic phases, grain boundaries, segregates, crystalline imperfections, impurities, etc. This difference in potential leads to the formation of anodic and cathodic areas on the metallic surface where oxidation and reduction reactions occur, respectively. These areas result in the formation of local action cells on the metallic surface. Local action cell can also be formed where there are variations in the environment or in temperature. The electrode potential is calculated from the Nernst equation:

$$E = E_0 + \frac{RT}{zF} In \frac{(ox)}{(red)} \qquad ---(8)$$

Where,

Eo = Standard electrode potential

R = Gas constatnt (1.98 cal/gm. Equivalent)

F = Faraday constant (96,500 coulombs/gm equivalent)

T = Absolute temperature

z = Number of the electrons transferred in the reaction

(ox) = Concentration of oxidised species (mol/L)

(red) = Concentration of reduced species (mol/L)

1.5 THERMODYNAMICS PRINCIPLES OF CORROSION

In most of the cases, metallic state represents the state of high energy. Therefore, metal have a natural tendency to react with other substances and go back to lower energy state with subsequent release of energy. All Metals show decrease in free energy by undergoing reaction with the environment, (except noble metals, which

are found in native state in nature), Thermodynamic stability of chemical compounds is determined by the signs and the change in the free energy (ΔG), when they are formed from simple substances.

Free energy is the thermodynamics property that express the resultant enthalpy of substance and its inherent probability. At constant temperature free energy can be expressed as follows:

$$\Delta G = \Delta H - T\,\Delta S \qquad ---(9)$$

where ΔG is the change the free energy, ΔH is the change in enthalpy, ΔS is change in entropy and T is absolute temperature.

When the reaction are at equilibrium then:

$$\Delta G^0 = -RT \ln Keq \qquad ---(10)$$

Where ΔG^0 is standard free energy, R is gas constant and Keq is equilibrium constant. The potential of a reaction is related to its free energy (ΔG) by:

$$\Delta G = -z\ FE \qquad ---(11)$$

A negative value for the free energy corresponds to a spontaneous reaction, whereas a positive value of ΔG indicates that the reaction has no tendency to proceed. The change in free energy accompanying an electrochemical or corrosion reaction can be calculated from a knowledge of the cell potential of the reaction. It is the redox potential by which one can predict whether a metal will corrode in a given environment or not.

1.6 POTENTIAL - pH DIAGRAM

To overcome some of the limitations of the e.m.f. and galvanic series, a system showing the effect of both potential and pH has been evolved by Pourbaix in the form E/pH diagrams. These diagrams, often called Pourbaix diagrams or potential – pH diagrams, are plotted for various equilibria on normal Cartesian coordinates with potential on vertical axis or ordinate, and pH on horizontal axis or abscissa. The diagram takes account of electrochemical and chemical equlibria of metals in

chemical equilibria of metals in conjunction with water, and since there are several such equilibria for each metal, only one metal can be already represented on one diagram. Such diagrams, are constructed using electrochemical calculation based on solubility data, equilibrium constants and the Nernst equation. The potential –pH diagram for iron exposed to water has been shown in Figure 1.1. It is necessary to conside the following equlibria before drawing the potential diagram for iron:

$Fe \rightleftharpoons Fe^{2+} + 2e^-$	Corrosion reaction	---(12)
$Fe^{2+} \rightleftharpoons Fe^{3+} + e^-$	Oxidation reaction	---(13)
$Fe(OH)_3 + 3H^+ + e^- \rightleftharpoons Fe^{2+} + 3H_2O$	Precipitation reaction	---(14)
$Fe^{2+} + 2H_2O \rightleftharpoons Fe(OH)^{2+} + 2H^+$	Hydrolysis reaction	---(15)
$2Fe + 3H_2O \rightleftharpoons Fe(OH)^{2+} + 2H^+$	Corrosion reaction	---(16)
$Fe + 2H_2O \rightleftharpoons HFeO_2^- + 3H^+ + 2e^-$	Corrosion reaction	---(17)
$HFeO_2^- + H_2O \rightleftharpoons Fe(OH)_3 + e^-$	Precipitation reaction	---(18)
$Fe^{2+} + 2OH^- \rightleftharpoons Fe(OH)_2$	Precipitation reaction	---(19)

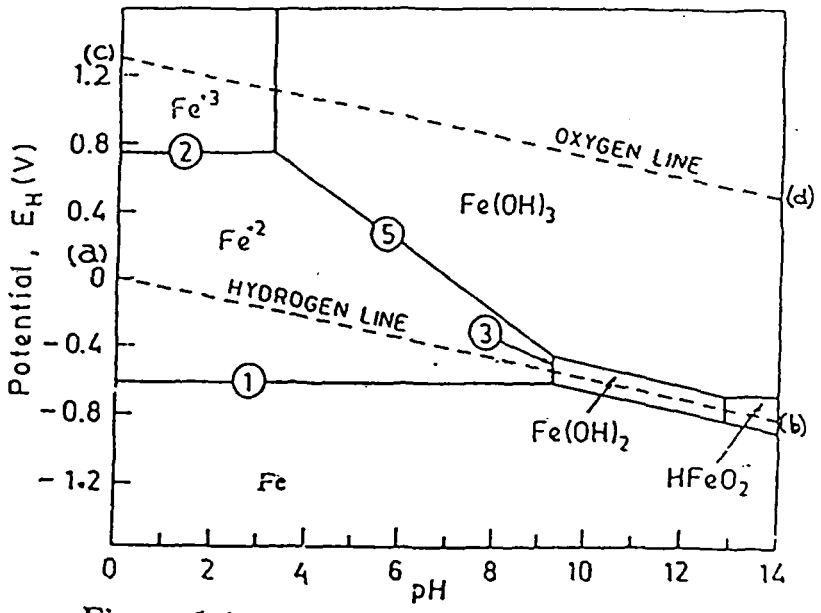


Figure 1.1 Pourbaix diagram for Fe-H_2O system at 25°C.

Reactions 12, 13 and 18 are independent of pH and are represented by straight horizontal lines; while reactions 14, 16 and 17 are dependent upon pH and potential and are represented by the Eh/pH plots by sloping lines. Reaction 15 and 19 which only depend on pH are represented by vertical lines. Oxygen is evolved above but not below (line "cd") in accord with the reaction:

$$H_2O \rightarrow \quad ½\ O_2 + 2H^+ + 2e^- \qquad \text{---(20)}$$

Hydrogen is evolved below but to above (line "ab") in accord with the reaction:

$$H^+ \rightarrow \quad ½\ H_2 + e^- \qquad \text{---(21)}$$

As can be seen in Figure 1.1 the redox potential of the hydrogen electrode (line "ab") lies above immunity region along all the pH scale. This means that Fe may be dissolve with evolution of hydrogen in aqueous solutions of all the pH values. In the pH interval (9.4 - 12.5), however, a passivating layer of $Fe(OH)_2$ is formed (reaction 20). At higher pH values soluble hypoferrite can form within a restricted active potential range. At a higher redox potential in the corroding medium, the passivating layer consist of $Fe(OH)_3$ or Fe_2O_3, nH_2O or Fe_2O_3 in different situations. Soluble ferrate (FeO_4^{-2}) can form in alkaline solutions at a very noble potential, but the stable field is not well defined.

Though the potential –pH diagram is quite useful in showing at glance specific conditions of potential and pH under which the metal will corrode, there are several limitations regarding their use in practical corrosion problems. Since the data in potential –pH diagram are thermodynamic, they convey no information about the rate of reactions.

The major use of such diagram, which can be constructed for all metals are:

i. Predicting whether or not corrosion will occur,

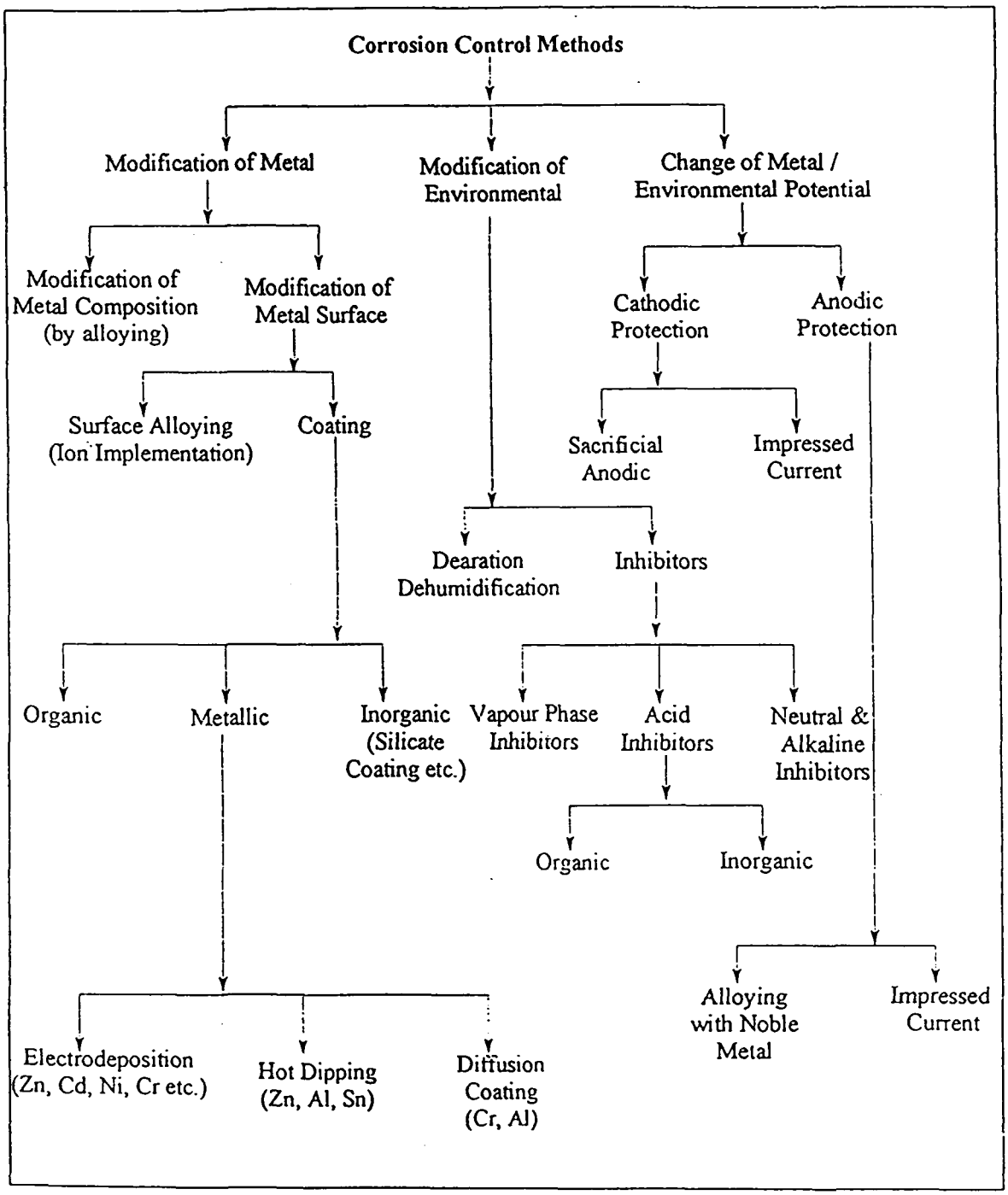
ii. Estimating the composition of corrosion products formed, and

iii. Predicting environmental changes, which will prevent or reduce corrosive attack.

1.7 METHODS OF CORROSION CONTROL

The methods of corrosion control are many and varied. Details of these various methods may be found in the extensive literature on corrosion control (13-15). The general classification of corrosion control methods is given is Table 1.3.

Table 1.3 Classification of corrosion control methods



1.8 PREVENTION OF CORROSION BY APPLICATION OF INHIBITORS

1.8.1 Definition of Inhibitors

The definition of an inhibitor favoured by the NACE is "a substance which retards corrosion when added to an environment in small concentrations" (16) and the recent ISO definition of an inhibitor is "chemical substance which decreases the corrosion rate when present in the corrosion system at a suitable concentration without significantly changing the concentration of any other corrosive agent" (17). Inhibitors may also be defined on electrochemical basis as substances that reduce the rates of either or both of partial anodic oxidation /cathodic reduction reaction.

From 19^{th} century onwards, vegetable wastes, plant extracts (18, 19) were used as inhibitors. Putilova et al. (20) have reviewed metallic corrosion inhibitors. Review on organic inhibitors (21-23) and organic sulphur compounds (24) have been published. Several books have been published on this subject (25,26). Besides, the university of Ferrara, Italy, conducts a symposium on corrosion inhibition once in five years (27). All the international seminars on corrosion discuss the developments and application of corrosion inhibitors (28). Various books on corrosion, review the subject in a precise manner (29).

1.8.2 Classification of Inhibitors

Inhibitors are classified in different ways. Depending on the environment, they are called acid inhibitors, neutral and alkaline inhibitors and vapour phase inhibitor. Depending on the mechanism of inhibition they are classified as cathodic, anodic and mixed inhibitors.

According to Putilova (20) inhibitors are of three types:

Type A: Those inhibitors, which function by forming a protective layer on the surface of metal, come under this type. Inhibitors of this type are commonly used and represent the largest class of inhibiting substances.

Type B: This type of inhibitors reduce the aggressiveness of medium towards the metal and may be called deactivators of the medium. These include sulphites (Na_2SO_3) which retard corrosion on water by combining with dissolved oxygen.

Type AB: Hydroxides or carbonates of the alkali metals (NaOH or Na_2CO_3) are added to water to prevent the corrosion of steel articles by lowering the hydrogen ion (H^+) concentration. A very thin film of insoluble iron hydroxide or carbonate is also formed on metal surface.

1.8.2.1 Acid Inhibitors

This may be further classified into inorganic and organic inhibitors.

i. Inorganic inhibitors

In strong acid solutions, Br^-, I^- have found to be effective inhibitors (30). The oxides like As_2O_3, Sb_2O_3 have been reported as inhibitors in acid media. These substances get deposited (31) in the form of metal on iron and increase the hydrogen over-voltage and subsequently reduce the corrosion. Recently addition of heavy metal ions like Pb^{2+}, Mn^{2+}, Cd^{2+} is found to inhibit corrosion or iron in acids. This effects is explained as due to under potential deposition of metal ions leading to complete coverage on the iron surface (32).

ii. Organic Inhibitors

The are organic substances containing N, S, or O as reactive centres though which they get adsorbed on the metal surface and inhibit corrosion of metals in acid environment. The prominent examples of acid inhibitors are acetylinic alcohols, aldehydes, mercaptans, hetroyclic compounds and thiourea derivatives (33,34).

An organic corrosion inhibitor can be anodic, cathodic or both depending on its reaction at the metal surface and how the potential of the metal is affected (35). Generally cathodic inhibitors increase cathodic polarization and shift the corrosion potential to more potential to more negative values, and anodic inhibitor enhances anodic polarization and shift the corrosion potential to more positive values.

The effectiveness of an organic inhibitor depends mainly on (i) Size (ii) Carbon chain length (iii) Bonding strength to metal surface. (iv) Aromaticity and or conjugated bonding (v) Nature and number of bonding atoms.

1.8.2.2 Neutral / Alkaline Inhibitors

These inhibitors include cathodic inhibitors (which increase cathodic polarization), anodic inhibitors (which enhance the anodic polarization) and mixed or general inhibitors (which act on both cathodic and anodic areas).

Anodic inhibitors forms are oxide or some other insoluble film. Insufficient concentration of anodic inhibitors will lead to severe pitting.

Sodium chromate is one of the most widely used and efficient inhibitors. Sodium silicate is generally used in hot water systems. The other compounds used in neutral and alkaline media are borates, molybdates and salts of organic acids like benzoates and salicylates.

1.8.2.3 Vapour Phase Inhibitors (VPI)

Those substances whose vapour pressure is sufficiently high act as vapour phase inhibitors. The vapour pressure of these compounds at room temperature is usually between 10^{-7} and 10^{-2} mm mercury, so that the inhibitors sufficiently fast to ensure its adequate availability in the vicinity of the metal surface.

The prominent examples of vapour phase inhibitors are amine based organic compounds and organic acid derivatives.

1.8.2.4 Anodic Inhibitors

The substances which retard the anodic area by acting on the anodic sites and polarize the anodic reaction are called anodic inhibitors. In the presence of anodic inhibitors, displacement in corrosion potential (E_{corr}) takes place in positive direction and suppress corrosion current (I_{corr}) and reduces corrosion rate. The curve E^{a}_{corr} represents the anodic reaction while E^{a}_{corr} represent the cathodic reaction and the point B where both anodic and cathodic reaction intersect corresponds to corrosion potential (E_{corr}) and corrosion current

(I_{corr}). The substances which retard the anodic reaction to enhancement of anodic polarization. In this situation, anodic curves become E^{a}_{corr} (Figure 1.2a) and the current E^{a}_{corr} corresponding to 0 is less than I_{corr} (corrosion current in the absence of the inhibitors) and the rate of corrosion is decreased. Anodic inhibitors which causes a large shift in the corrosion potential are called passivating inhibitors, if used in insufficient concentration, they cause pitting and sometimes an increase in corrosion rate.

Anodic inhibitors are of two types.

(i) Oxidising anodic inhibitors – They inhibit corrosion by passivating the metal surface eg. chromate, nitrite (36).

(ii) Non oxidising anodic inhibitors – They inorganic anions such as molybdate benzoate, phosphate are the examples of non-oxidising type anodic inhibitors.

These inhibitors slow down anodic reaction by forming passive film on the metal surface in presence of oxygen.

1.8.2.5 Cathodic Inhibitors

Those substances, which reduce the cathodic area by acting on the cathodic sites and polarize the cathodic reactions are called cathodic inhibitors. They displace the corrosion potential (E^{c}_{corr}) in the negative direction and reduce corrosion current, thereby retard cathodic reaction and suppress the corrosion rate (Figure 1.2b). In this situation, the point of intersection is at 0 and corresponding corrosion current (I^{c}_{corr}) will be lower than that without inhibitor (I_{corr}). The cathodic inhibitors, with a few exceptions (37) do not read to intensified or localized attack, since, cathode areas are not attacked during corrosion.

Cathodic inhibitors can be divided into three categories.

i) Cathodic poisons – The substances which interfere with the formation of hydrogen atoms or recombination of hydrogen atoms to H_2 gas are know as cathodic poisons e.g. arsenic and antimony salts.

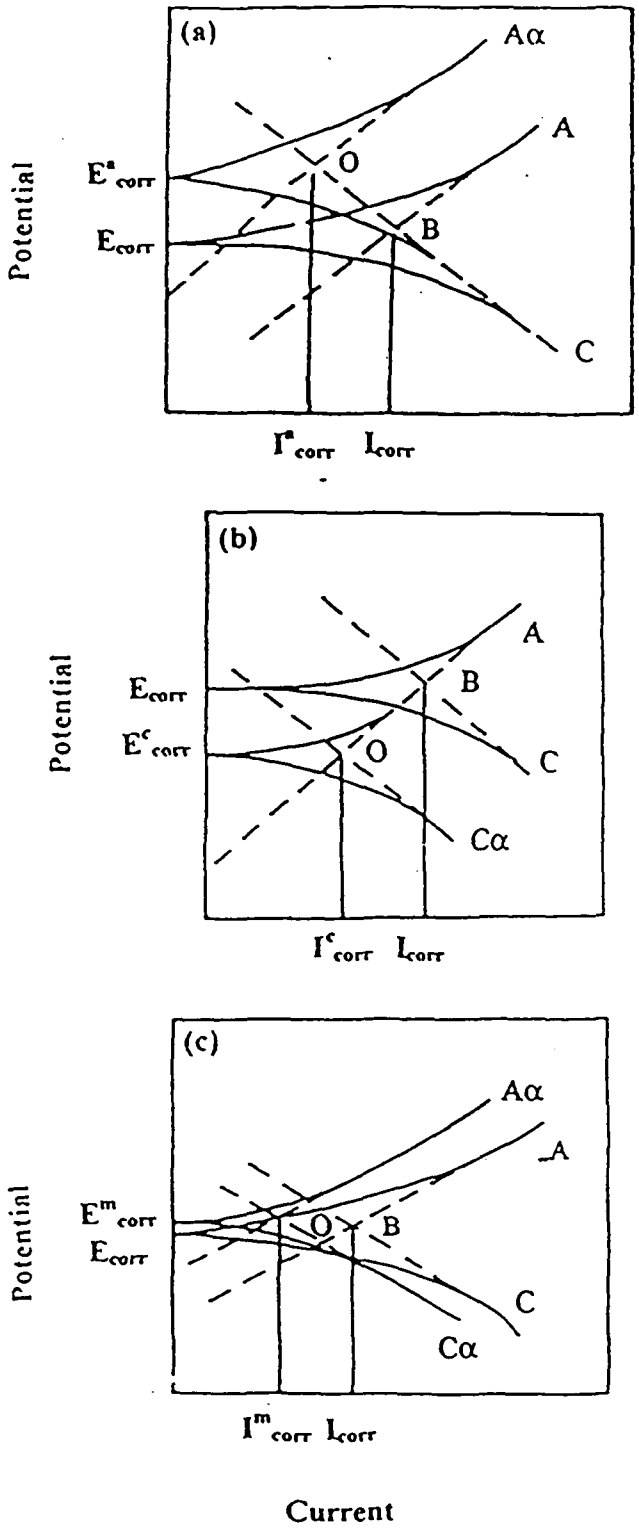


Figure 1.2 Mechanism of action of corrosion inhibitors based on polarisation effects.

ii) Oxygen scavangers – The substance which inhibit the corrosion by removing dissolved oxygen are called oxygen scavangers e.g. hydrazine and sodium sulphite.

$$2Na_2SO_3 + O_2 \rightarrow 2Na_2SO_4 \quad \text{----(23)}$$

$$N_2H_4 + O_2 \rightarrow N_2 + 2H_2O \quad \text{----(24)}$$

The advantage of hydrazine over sulphite is that it does not increase hardness of water, which in turn prevents scale formation in boiler.

iii) Cathodic precipitate (Filming inhibitor)-Calcium bicarbonate and zinc sulphate are the example of filming type inhibitors. The cation parts of these inhibitors migrate towards cathode and react with cathodically formed alkali to produce insoluble protective film on cathode and thereby inhibit cathodic reaction.

$$Ca^{++} + 2HCO_3^- + OH^- \rightarrow CaCO_3 + HCO_3^- + H_2O \quad \text{----(25)}$$

$$Zn^{++} + OH^- \rightarrow Zn(OH)_2 \quad \text{----(26)}$$

1.8.2.6 Mixed Inhibitors

There are a number of inhibitors which inhibit corrosion by interfering with both the anodic and cathodic reactions and are called mixed inhibitors. This type of inhibition can be represented by Figure 1.2c. The anodic and cathodic reaction are represented by $E^m_{corr}A$ and $E^m_{corr}C$ respectively and corrosion current I^m_{corr} in presence of such type of inhibitors in considerably less than that in their absence. Gelatin, Glue and other high molecular weight substances fall in this category. Machu (38,39) claims that there is mainly due to formation of porous layer which increases the electrical resistance of the surface layer.

1.8.3 Influence of Inhibitors on Corrosion Reaction

An inhibitor may decrease the rate of anodic process, the cathodic process or both processes. The change in corrosion potential on addition of the inhibitor is the indication of a retarded process (33). Shift of the corrosion potential in the positive

direction indicates mainly retardation of the anodic process (anodic control) whereas shift in the negative direction indicates retardation of the cathodic process (cathodic control). Little change in the corrosion potential suggests that both anodic and cathodic processes are retarded.

In the presence of an inhibitor, a shift of polarization curves without a change in the Tafel slope indicates that the adsorbed inhibitor acts by blocking active sites so that reaction cannot occur rather than affecting the mechanism of the reaction (40). A change in the Tafel slope is the indication of affecting the mechanism of the reaction.

1.9 TECHNIQUES FOR CORROSION INHIBITION MONITORING

The various techniques employed for corrosion monitoring have been classified as:

i. Non-Electrochemical Methods.

ii. Electrochemical Methods

i. Non-Electrochemical Methods

These include techniques like weight-loss measurement and gasometric methods. The main disadvantage of these methods is that these require relatively long exposure times of the corroding systems. Also the non-electrochemical methods are in general restricted to systems which do not form adherent layer of corrosion products.

a. Weight Loss Measurements

This methods is the most reliable method. The electrochemical measurement results are usually compared with weight loss data. Here the change in weight of the specimen is determined by immersing the specimen in the corrosive medium for a fixed time. The rate of metal removal due to corrosion is calculated from:

$$CR = KW/ATD$$

where CR is the corrosion rate, K is a constant, W is the weight loss to the nearest 0.0001g., A is the area of the specimen to the nearest 0.01 sq. cm., T is the time exposure to the nearest 0.01 hour and D is the density in g/cu.

A variety of units have been used in the literature to express the corrosion rate. Using the units for T, A, W and D in the above equation corrosion rate can be calculated in different units with the appropriate value of K (Table 1.5). If desired, these constants may also be used to convert corrosion rates from one set of units to another. To convent corrosion expressed in unit x to a rate in unit y, multiply by K_y/K_x. e.g., if R is 10 mpy the rate in mm/yr would be:

$$10\ (8.76 \times 10^4/3.45 \times 10^6) = 0.254\ \text{mm/yr}.$$

Table 1.5 Values of constant K, for determining corrosion rate in different units using weight loss measurements

S. No.	EXPRESSION	DIMENSION	CONSTANT K
1.	Inches per month, imp	in/mo	2.87×10^2
2.	Inches per year, ipy	in/yr	3.45×10^3
3.	Miles per year, mpy	mils/yr	3.45×10^6
4.	Millimetres per year, mm/yr	mm/yr	8.76×10^4
5.	Micrometre per year, mm/yr	μm/yr	8.76×10^7
6.	Picometre per second, pm/sec	pm/sec	2.78×10^6
7.	Micrograms per square metre per sec., mg/(sq m) (sec)	μg/(s qm) (sec)	$2.78 \times 10^6 D$
8.	Milligrams per square decimetre per day, mdd	mg/(sq dm) (day)	$2.40 \times 10^6 D$
9.	Grams per square metre per hour, g/(sq m) (hr)	g/(sq m) (hr)	$1.00 \times 10^4 D$

b. Gasometric Methods

This methods yield reliable and accurate with a high degree of reproductivity. In this method the volume of hydrogen gas (in acid corrosion) involved during a corrosion reaction is directly measured at a constant temperature. The corresponding metal loss can be calculated. This technique has been used for the inhibitors studies by Nathan (41). Mathur et al (42) have designed a gasometric unit with which corrosion rates could be monitored under controlled conditions of temperature the pressure without any aqueous correction. Singh et al. (43) have designed apparatus for measuring adsorbed hydrogen gas and hydrogen diffusion. Also this technique has been successfully applied for the determination of corrosion kinetic parameters by them.

However this technique has certain limitations such as it can be applied to a strong oxidising medium like nitric acid, to systems where the inhibitor used undergoes reduction with the hydrogen gas evolution, etc.

ii. Electrochemical Methods

The electrochemical methods are most widely used for the study of inhibitors. Electrochemical methods are finding increased use in corrosion research and in engineering applications. Such methods are practical because the corrosion behavior of material-electrolyte combinations is a direct function of the mechanism as well as kinetics of the electrochemical methods can be used, in field or in laboratory, to measure corrosion rates without removing the specimen from the environment or altering the sample itself.

a. Polarization Methods

The electrochemical polarization of metallic sample is accomplished with a power supply known as potentiostat. An auxiliary electrode supplies the current to the working electrode (test specimen) in order to polarize it. The potential between the working electrode and reference electrode is monitored or set at a fixed value. Figure 1.3 illustrates schematically a typical experimental arrangement.

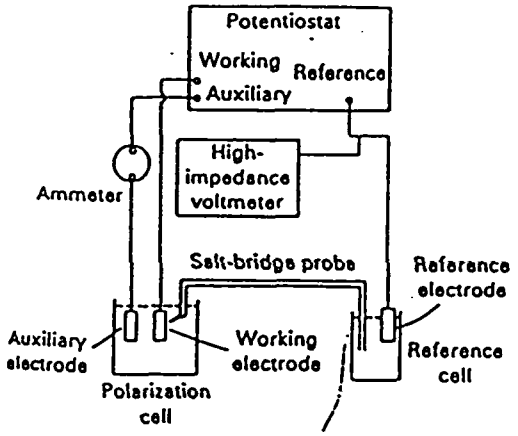


Figure 1.3 Instrumental setup for electrochemical polarisation experiments.

The system is designed so that only an extremely small current can pass between the reference electrode and the working electrode. The current needed to polarize the working electrode is supplied from the auxiliary electrode. Several American

Society for Testing and Materials (ASTM) standards discuss methods for performing these experiments (44,45).

In this method the behavior of inhibitor is understood by drawing a Tafel plot (Figure 1.4) in absence and presence of inhibitor. The percentage inhibition is calculated from the formula.

$$IE\% = \frac{I^{o}_{corr} - I_{corr}}{I^{o}_{corr}} \times 100 \qquad \text{---(27)}$$

I^{o}_{corr} = Corrosion current density (corrosion rate) in absence of inhibitor,

I_{corr} = Corrosion current density (corrosion rate) in presence of inhibitor.

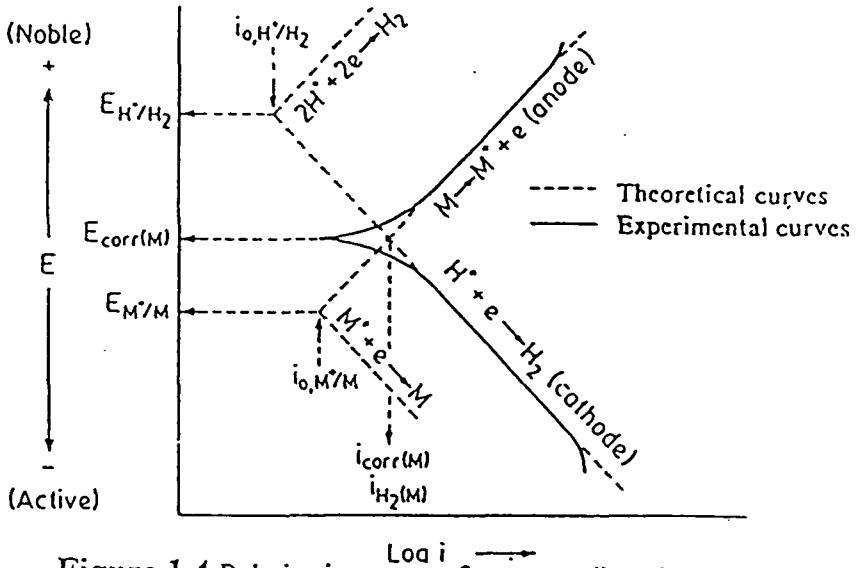


Figure 1.4 Polarisation curves for a corroding electrode.

E_{corr} = Corrosion potential
i_{corr} = Corrosion current

The corrosion rate is determined from the polarization data in two way:

1. Tafel extrapolation method
2. Linear polarization method.

In Tafel extrapolation method the linear portion of the Tafel curve is extrapolated. The point of intersection is referred to as I_{corr}.

Linear polarization method provides the value of absolute corrosion rate from the following relation.

$$I_{corr} = \frac{\beta_a \times \beta_c}{2.3\,(\beta_a + \beta_c)} \times \frac{1}{R_P} \qquad \text{---(28)}$$

Where β_a and β_c are Tafel constants, $1/R_P = \Delta I / \Delta E$ = polarization conductance.

ii. Impedance Method

The impedance technique (46-49) has become a popular tool for the measurement of corrosion rate in recent years. In this technique a small amplitude perturbation is applied to the working electrode at a number of discrete frequencies. At each of these frequencies the resulting current waveform will exhibit a sinusoidal response that is out of phase with the applied potential signal by a certain amount.

The main advantages of this method are:

i. applicable to low conductivity systems,

ii. provides mechanistic information,

iii. solution resistance is completely eliminated.

The inhibition efficiency of the inhibitor can be determined from AC impedance method (50, 51) by the following formula:

$$IE\% = \frac{1/R_{to} - 1/R_t}{1/R_{to}} \times 100 \qquad \text{---(29)}$$

R_t and R_{to} are the charge transfer resistance with and without inhibitor.

For determination of R_t, very small potential is applied as a function of frequency (usually 60 KHz-1mHz). The impedance of the corroding system for various frequencies can be measured using lock-in-ampifier. A plot of Z (real) vs Z" (imaginary) for various frequencies given a semicircle (Nyquist plot) which cuts the real axis at higher and lower frequency it corresponds to ($R_s + R_t$). The difference

between the two values gives R_t. From R_t the corrosion current can be calculated using Stern-Geary equation:

$$I_{corr} = \frac{\beta_a \times \beta_c}{2.3\,(\beta_a + \beta_c)} \times \frac{1}{R_t} \qquad \text{---(30)}$$

The double layer capacitance can be determined from the frequency at which Z" is maximum from the relation:

$$Fz''_{max} = \frac{1}{2\pi\, C_{dl} \times R_t} \qquad \text{---(31)}$$

1.9.1 OTHER METHODS

The methods such as Radio tracer technique (52), Spectroscopic methos (53-55), X-ray phoyo electron spectroscopy (56), Auger electron spectroscopy (57), Ellipsometry (58), Hydogen permeation (59), Quartz crystal method (60), Electrochemical noise method (61), have also been used for study the inhibition phenomenon.

1.10 CORROSION INHIBITION BY VAPOUR-PHASE CORROSION INHIBITORS (VCIs)

The process of atmospheric corrosion is natural action of a material, in most cases a metal, returning to its original state through an electrochemical process caused by a reaction with the surrounding environment. Even though it is a natural process, there are certain environmental conditions to which metals are exposed during manufacture, processing, storage or shipment that can aggressively accelerate the degradation. In normal atmosphere containing pollutants, metals begin to corrode at this accelerated rate when the relative humidity of the air layer next to the surface exceeds about 75%, mostly in coastal areas where the main factor of corrosion is the presence of chloride ion (62-65). Acid rain, hydrogen sulphide, nitrogen dioxide and sulfur dioxide, temperature also accelerate corrosion (66-68).

There are several ways to prevent atmospheric corrosion. While methods such as the use of an inert atmospheric, dehumidification, or coatings are fine in some applications, they may not be appropriate in others because of cost and practicability. The use of vapour phase corrosion inhibitors (VCIs) is an effective and relatively inexpensive method of controlling corrosion problem in closed systems or environment. Vapour phase corrosion inhibitors (VCIs) also known as volatile corrosion inhibitors (VCIs). Vapour phase corrosion inhibitors are organic compounds that have sufficient vapour pressure about 10^{-7}-10^{-2} mmHg (69).They are transported by diffusion through gas phase and adsorb onto the metal with a thickness of few monolayers, thereby protecting it from corrosion. VCIs are especially useful for protecting metals in cavities and other hard to reach.

According to Miksic and Miller, " vapour phase corrosion inhibitors are secondary electrolyte layer inhibitors that posses appreciable saturated vapour pressure under atmospheric conditions, thus allowing vapour-phase transport of inhibitive substance (70).The inhibitor is transmitted as vapours, and the vapours phase is controlled by the structure of crystal lattice and the nature of atomic bond in the molecule. The protective vapour expand within the enclosed space until the equilibrium determined by their partial pressure of the vapour is reached. The higher the vapour pressure, the sooner the saturation of protected space. For practical purposes, it is preferable to use less volatile inhibitors that provide long-lasting and durable protection over periods of 2 years to 3 years and protection of breathable enclosures and enclosures where changes of local atmosphere occur.

The efficiency of a vapour phase concession inhibitor depends on its ability to be adsorbed on the metal surface, strength of this adsorption and temperature dependence of its vapour pressure. Each of these properties depends on the chemical structure of the inhibitor (71).

Bastidas et al. (72) discussed the parameters of volatile corrosion inhibition process on into sections transport of VCI to metallic surface, vapour pressure of a VCI, dependence of vapour pressure upon temperature, effect of pH on VCI behaviour, formation and destruction of adsorbed film, and VCI monitors .

Andreev and Knznetsov (73) studied the characteristic features of metal protection by volatile corrosion inhibitors with effect of their chemical structures. Andreev and Knznetsov (74) analysed the influence of heat transfer on metal protection with volatile corrosion inhibitors, the mechanism of corrosion initiation, and methods for its prevention.It was found that effective VCIs can be prepared from substances that azeotropic mixtures with water.

Volatile corrosion inhibitors (VCIs) evolved over the years to serve as effective protection for metals exposed to marine environments, chemical processing, metalworking, and many other corrosive conditions. A new class of nontoxic and nonpolluting VCIs that can be safely used in environmentally sensitive areas (75).

Prenosil (76) studied that volatile corrosion inhibitors, combined with sulfonates (contact corrosion inhibitors), can retard corrosion in several different coating systems.

Prabhu-Gaonkar and Kamat (77) carried out the experimental work to identify effective volatile corrosion inhibitors as an admixture in repair mortar adopting to Indian tropical conditions.

Murav'eva et al. (78) synthesized aliphatic tertiary diamine (ATD) and tested by gravimetric and electrochemical methods as a film-forming inhibitor of hydrogen sulphide corrosion. Both H_2S-induced general corrosion in the vapour and liquid phase and hydrogenation are inhibited by ATD more effectively than aliphatic tertiary amines and commercial corrosion inhibitors.

Roserfeld et al. (79) studied the effect of structure and the influence of substituents (OH, NO_2, NH_2) on the effectiveness of inhibitors. It was shown that for ferrous metals, aromatic nitrogen bases were ineffective corrosion inhibitors, even when additional hydroxyl or nitro groups were introduced. The majority of strong bases of aliphatic and alicyclic compounds were effective vapour phase corrosion inhibitors. He found that cyclohexylamine, hexamethyleneime, piperidine, morpholine and benzylamine were the most effective bases. It was claimed that the effectiveness of benzoates could be increased by the introduction of a highly electrophilic nitro group into the ortho position or two nitro groups into the meta positions with respect to the carboxyl group. These group reduce the electron density in the aromatic ring.

Miksic (80) claimed that nitro group, induced polarization shifts the steady-state potential of the metal in the positive direction, inhibiting the anodic reaction. Compounds that cause reduction of the nitro group increases the oxidising properties of the inhibitor.

Trabanelli et al. (81) listed the inhibiting efficiency values of various aliphatic, alicyclic and aromatic amines as VCIs. He concluded that aliphatic and alicyclic compounds show inhibiting efficiencies superior to those of the aromatic substances having similar vapour pressure.

Trabanelli et al (82) in a further attempt correlated the inhibitors efficiency with the adsorption phenomenon involves the availability of electrons on the atom or atoms considered as reaction centres for the formation of the metal inhibitor bond. Naturally, the steric factors can also playa determining role on the inhibitor's action.

Singh and Banerjee (83) categorized VCIs according to application to various metals, such as ferous and non-ferous metals and alloys.

Miksik (84) investigated several VCIs that are very effective in providing corrosion inhibition and also formulated from biodegradable environmentally friendly raw materials, manufactured from renewable resources

Iwanow et al. (85) investigated the vapour phase corrosion inhibitors and their possible application for the protection against corrosion in many types of technical objects such as internal spaces of steam and water power and refinery plants as well as in enclosed cavities of steel structures (bridges, ships, pylons etc).

Ashish Gandhi (86) examined volatile corrosion inhibitors can protect the bottom of storage tanks used in the oil and petroleum industries. These systems can be used in conjunction with traditional corrosion central method of catholic protection. Ashish Gandhi (87) described the application of volatile corrosion inhibitors in boiler and cooling towers.

Zhang et al. (88) discussed vapour phase rust proofing technology and its application for protection of off-stream thermal power equipment including the introduction of vapour phase inhibitors and carries for the inhibitors.

The possibility of a vapour phase corrosion inhibitor, cyclohexylamine carbonate (CHC) for protecting chemical equipment was studied by Wei Gang et al. (89). The results showed that CHC can provide good protection for chemical equipment in the vapour saturated environment. CHC was considered a physical adsorption inhibitor, which was suitable for enclosed system.

Hara Yuichi (90) investigated the compound containing ethylene polymers, which are cross-linked with silane after extrusion and volatile corrosion inhibitors, which prevented discoloration of a Cu sheet and exposure to 65^0C/95% humidity for 12h showed gel content 60% after heating ethylene at 100°C for 24h.

Erwin et al. (91) studied the corrosion inhibiting properties of some aliphatic amines containing $C_{12\text{-}21}$ amines on metal parts of dryers.

Barry and Chandler (92) investigated a film of VCIs for protection of electronic equipment.

Alink et al. (93) investigated a method for vapour-phase corrosion inhibition and transport of inhibitor in the vapour phase to subsequent liquid corrosion sites in a gas lift process in which a lift gas is pumped into a well to facilitate petroleum production of the well comprises introducing to the lift gas an inhibiting amount of a dihydrothiazole.

Moerdijk et al. (94) studied reaction products of volatile weakly alkyl substance and volatile weak acid. The inhibitors were mainly used for protection of metals and alloys in electronics and chemical process industry.

Chandler et al. (95) prepared biodegradable polyester plastic films (polymers resins) containing vapour phase corrosion inhibitor for the packaging and protection of metallic surfaces. These film are further characterize in that (a) the vapour-phase corrosion inhibitor is selected from amine salts, ammonium benzoate, triazole derivatives, alkali dibasic acid salts, alkali nitrite, tall oil imidazolines, alkali metal molybdates and their mixtures and is present in an amount of < 25% of the polymeric resin; and (b) the biodegradable resin products are blended with a suitable polymeric resin to provide finished products containing 1-3% VCIs.

A plastic component containing a corrosion inhibiting component (VCI) and a resin is also provided wherein the corrosion inhibiting component includes 0.13% to 1.25% alkali metal nitrite, 1 % to 5.63% alkali metal benzoate and 0.25% to 3.13% alkali molybdate by weight of plastic component. The plastic component can be formed into a film can be used to cover metal article thereby preventing corrosion (96).

Shapira et al. (97) examined the composition or premix based on volatile corrosion inhibitors useful for protecting metal parts against corrosion.

Masao et al. (98) investigated anti-rusting metal- packaging films comprise a-olefin-based polymers and volatile corrosion inhibitors, with good property retention under high temperature 50°C and relative humidity 90%.

Henderson et al. (99) studied water-resistant multilayer anticorrosion polyolefin composite sheet, useful as packaging materials for metal during storage and transportation. comprises a high strength, tear resistant and flexible polyolefin scrim low density polyolefin layer which is impregnated with a vapour corrosion inhibitor (VCI) in solid form, bonded to the bottom surface of the scrim and a polyolefin barrier layer bonded to the upper surface of the scrim to reduce the transmission of water, water vapour, oxygen and other environmental gases through the composite material.

1.10.1 Protection of Ferrous Metals

Amine and amine salts effectively protect ferrous metals. Their inhibiting action is generally found to improve with increase in molecular size of the amines. Dicyclohexylamine and its salts (100-102) and other amines (100) are well known atmospheric corrosion inhibitors for ferrous alloys.

In a recent paper Kuznetsov et al. (103) studied the effect of volatile (IfKhAN-118) and contact inhibitors (aliphatic primary amine, dipheylguadine (DPG), and a quaternary ammonium salt (QAS) and their mixtures on corrosion and electrochemical behaviour of carbon steels in a aqueous electrolyte. Kuznetsov et al. (104) also studied the inhibitive effect modified by more hydrophobic aliphatic amines in carbon dioxide under conditions of periodical wetting proved to be enhanced. New inhibitors, namely amine A and IfKhAN-72, are effective against

cabon dioxide corrosion and retain their aftereffects for a long period of time.

Da-quan Zhang et al. (105) developed a novel volatile corrosion inhibitors (VCI), bis-piperidiniummethyl-urea (BPMU) for protection of carbon steel. Its vapor corrosion inhibition property was evaluated under simulated operational conditions. The structure of protective film on metal surface, which was suggested as one BPMU molecule chelated with one Fe atom to form a complex with two hexa-rings. Zhang et al (106) also developed a morpholinium oligomer (MPO) as a vapour phase inhibitor for protection of mild steel. The different polar groups of MPO had synergistic adsorption.

Subramania et al. (107) synthesized diethylamine phosphate and evaluated its inhibitive performance on steel components through accelerated vapour phase corrosion test and electrochemical methods such as Tafel polarization and impedance measurement at 100% RH in a confined space. The performance of VPI in different environments such as chloride, sulfur dioxide and field test also evaluated.

Bastidas et al. (108) studied the action of two vapour phase inhibitors, dicyclohexyl-ammonium nitrite (DICHAN) and dicyclohexylamine (DICHAMIN), on the atmospheric corrosion of mild steel at a relative humidity of 100 % and under isothermal condition (25^0C). In order to obtain electrochemical data within adsorbed moisture a layers of vapour phase inhibitor monitor (VIPM) was developed. The test carried out revealed that the corrosion rate of mild steel decreases in the presence of DICHAN and DICHAMIN. With the VIPM and electrochemical technique used it is possible to understand the inhibition mechanism of these two vapour inhibitors on the atmospheric corrosion of steel.

Andreev et al. (109) studied the protection of steel by the conditions of the formation of adsorbed VCI layers in cabon dioxide atmosphere. Andreev et al (110) also studied the effect of chemical nature of amines on the protective properties of their solution against corrosion of steel in vapour phase conditions.

Ramzan kahraman (111) studied the effectiveness of sodium benzoate as an inhibitor to slow down or prevent atmospheric corrosion of mild steel during storage in Arabian Gulf region. Corrosion test was evaluated through weight loss

determination and electrochemical technique. Treatment of steel with sodium benzoate lowered its corrosion rate during initial days of its exposure to atmosphere.

Vuorinen et al. (112) investigated carboxylates salts of amines as vapour phase corrosion inhibitors for mild steel. These compounds showed effectiveness in excess of 90%. Morphaline was the most effective amine and caprylic acid the most effective acid constituent.

Wei Gang et al. (113) examined dichyclohexylamine nitrite was a chemisorbing inhibitor useful for rust prevention on steel and is used for sealing systems.

Chandler (114) developed biodegradable volatile corrosion inhibitor in harmony with concern for the environment. While these chemicals offer excellent protection to metal surfaces, they have a low impact on the environment. Corrosion protection and effect on environment of two of these amine containing inhibitors for the corrosion of carbon steel were studied, corrosion and toxicity testing demonstrated that the compounds not only provide excellent corrosion protection but also have low toxicity level when placed in a marine environment.

Yu. I. Kuznetsov et al. (115) studied the corrosion behaviour of stainless steel type-3 in hydrogen sulfide media. The inhibition effects of a volatile, water soluble inhibitors (IPKHAN 72) and the starting aliphatic amines for its synthesis were compared. IPKHAN 72 was more effective especially in the presence of CO_2. In CO_2 free hydrogen sulfide media, IPKHAN 72 functions as an anodic inhibitor. In the presence of CO_2 it also declerates the cathodic process.

Quraishi et al. (116) synthesized a new family of vapour phase corrosion inhibitors comprising of six members by the reaction of a heterocyclic base, formaldehyde and ketones. The inhibiting action of these compound has been evaluated for corrosion of mild steel at 100% relative humidity after 30 days by weight loss and potentiodynamic polarisation methods. Inhibitors containing piperidine exhibited better performance than those containing morpholine and dimethylamine. Potentiodynamic polarization studies have revealed that all the compounds are predominantly anodic in nature.

Subramanian et al. (117) studied the corrosion inhibiting behaviour of morpholine

and its salts such as carbonate, borate and phosphate on mild steel at 40°C in 100% RH using modified cell design and other methods. Of these morpholine and its carbonate salt exhibited 90 and 85% IE respectively, whereas the other salts showed less than 40% I.E.

Marczak et al. (118) synthesized the oxazolidine derivatives (as vapour phase corrosion inhibitors for steels) are produced by condensation of N-methylethanolamine with aliphatic aldehydes in equimolar amounts in the presence of a neutral organic solvent. Preferably the resulting produces are purified by vacuum distillation. Optionally, the products are dissolved in an oil base.

Leng et al. (119) investigated the inhibition mechanism of a typical vapour phase inhibitor (ammonium benzoate) on iron under atmospheric corrosion conditions. It showed that the rate of the anodic and cathodic partial reactions of the corrosion process are strongly effected by the thickness of the electrolyte layer. Due to presence of the inhibitor the surface is passivated.

Vuorinen et al. (120) found cyclohexylamine sorbate/borate, morpholine laurate/zelate/sebcate/thiophenolate and morpholine mannich base derivatives to be effective VCIs for steel.

Bactides et al. (121) evaluated the inhibiting action of dicyclohexylammonium nitrite and dicyclohexylamine for corrosion of steel at 100% relative humidity.

Naphtheone vapour at 250-350 ^{0}C found to be effective VPI for steel in HCI vapours (122).

Lee Bum Sung et al. (123) studied the effect of additions of various binders, fillers and reducing agents on the protective action of a volatile inhibitor based on hexamethylene tetramine in corrosion of iron and its alloys in humid atmosphere.

Effect of several volatile inhibitors based on dicyclohexylammonium nitrite, amino compounds e.g. hexamethylene tetramine, Pb, Ca and AI Stereates and aromatic and alphatic acids on atmospheric corrosion (90% RH at 40°C) of cold rolled iron has been studied by Asahara Ternzo et al (124).

A composition containing $NaNO_2$ triethanol amine and a low molecular weight

surfactant e.g. napthethanic or aliphatic have been found to be highly effective in field test for ferrous alloys (125). Here surfactants act as wetting agent and substantially improve effectiveness of compositions.

Acylation product of lanolin or multi basic alcohol as pentaerythritol, glycerol, sorbitol etc. dissolved in oils, kerosine or organic solvents have been reported to protect iron and steel in humid atmosphere (126).

Saverina et al. (127) patented a formulation comprising of aliphatic amines RCH:NR' (R and R' = alkyl group) which protects steel in acid and NaCl atmospheres.

1.10.2 Protection of Copper and Copper Alloys

It is well known that an inhibitor effective for one metal can stimulate attack or be ineffective on some other metals and alloys. Thus Dicyclohexylammonium nitrites (Dichan) which were potentially effective for iron an steels accelerate the attack on copper and its alloys e.g. brass and bronze.

Triazole based compounds were well known vapours as well as liquid phase corrosion inhibitors for copper metal and its alloys.

Benzotriazole and tolyltriazole have been reported to have excellent inhibitory effect on copper and its alloys (128).

Cyclohexylamine chromate (129) and thiourea derivatives particularly phenylthiourea (130) have been found to protect corrosion of brass.

Barbior and Fiard (131) observed that acetylenic alcohols to have considerable inhibiting effects on atmospheric corrosion of copper. Treatment of powdered copper with an aqueous solution of gelatine gave reliable protection against oxidation between operations and also improved corrosion resistance during storage (132).

Losev and Plisov (133) observed the inhibiting effects of silicons amines e.g. dimethylaminomethyl triethoxysilane on atmospheric corrosion of copper. During the kinetic studies, they have observed on inflection point on the kinetic curves on transition from corrosion promotion to retardation. This has been explained by

taking into account the dual role of silicones amine intensify corrosion of copper by forming complexes followed by hydrolysis of these complex compounds resulting in the formation of hydrophobic surface films of silicons which retard further corrosion.

An aqueous solution of 5-50% complex phenol carboxylic acid or its ester (tannic, catechuic, caffeic, gallic, guinic, protectatechuic, chlorogenic, tannin) and 0.1-20% water soluble heterocyclic compounds such as ethylene thiourea, mercptobenzothiozole, 2-aminobenzimidazole or 2-aminobenzothiazole have been reported to protect copper corrosion in aggressive environments during storage (134).

1.10.3 Protection of Silver

Silver is stable in reducing atmospheres and reacts vigorously in oxidising environments e.g. containing NO_3 due to formation of non-protective complex of silver. It is also very succeptible to attack by most sulphur compounds getting tarnished with a yellow, brown or black sulphide film. This metal is protected from H_2S atmosphere by enclosing in paper impregnated with copper or zinc compounds. These materials are not vapour phase inhibitors in strict sense as they adsorb gaseous sulphur compounds to prevent reaction with silver metal.

Dohi Nobuyasu et al. (135) reported benzotriazole has an inhibiting effect on silver metal in H_2S atmosphere. It has been suggested that the protective action of this inhibitor on the metal is due to the formation of protective layer on the metal surface which may be a complex of silver.

Solution of chlorobenzotriazole in a polar solvent such as alcohol, ketone, glycol impregnated in packaging paper or the metal treated with this solution effectively protects the metal in H_2S atmosphere (136).

Polukarov (137) proposed a composition based on organic compounds for protecting the surface of Ag against tarnishing associated with atmospheric corrosion in the presence of water vapour and hydrogen sulphide. The organic compounds contain higher fatty acids preferably stearic acid or ethylene glycol monostereate at conc. 3-5% and also a non-polar organic solvent preferably CCl_4.

Organosilicate compounds e.g. phenyl aminoethylene methyl dithoxisilane, 1-aminohexamethylene triethoxisilane and diethylaminomethylene triethoxisilane were found to have an inhibiting effect on silver coated on steel (138). The protector was applied by quickly dipping specimen into alcoholic solution of the inhibitors. Accelerated atmospheric corrosion test performed in NaCI and $MgCI_2$ vapours at 60°C showed considerable inhibition.

1.10.4 Protection of Aluminium

Aluminium metal is very susceptible to attack in saline atmosphere. Vapour of some nitrogen containing compounds particularly amino compounds and composition of two or more than two compounds are reported to have inhibiting effects towards corrosion of aluminium and its alloys. Some amines are reported to have protective actions on aluminium in HCI vapours (139).

Mixtures of hexamethylene tetramine and $NaNO_2$ prepared as inhibited paper, powder or tablets were tested on aluminium specimens exposed in an atmosphere with 90% relative humidity at 40°C (140). The 1:4 mixture provided the best protection. Addition of 6% milk casein or 7% gum Arabic to this composition improved the protection.

The effect of various binders on inhibiting properties of hexamethylene tetramine on aluminium corrosion in humid atmosphere has been reported (141). Of the various binders used the most pronounced effect is observed by polyvinyl alcohol (5-7%), milk casein (8-10%) and gum arabic (9-10%).

1.10.5 Protection of Ferrous and Non-ferrous Metals

In order to develop a universal inhibitor which may protect ferrous as well as non-ferrous metals enormous amount of work had been done all over the world and indeed many formulations have been suggested.

Poongothai et al. (142) investigated highly volatile wood bark oils used as a vapour phase corrosion inhibitors for mild steel and copper in sodium chloride and sulphur dioxide environments. The inhibition efficiency of these wood bark oils examined by using weight loss, potentiodynamic polarization and a.c impedence spectroscopic

methods. It has been found that the inhibition capability of these oils increases with increase from 0.4 to 4% in concentration. The results indicated that the bark oils have significant inhibitive effect. This is due to adsorption of inhibitor molecule on the metal surface. It has also found that 4% concentration of these inhibitors offered, above 90% inhibition efficiency for both mild steel and copper.

Georg Reinhard et al. (143) studied a sublimation-capable corrosion inhibiting mixture containing an aromatic mercaptothiazole, a water soluble multiple-substituted phenol, L-ascorbic acid or its salts and optionally a carboxylic acid/salt combination is suitable as a vapour phase corrosion inhibitor for protection of ferrous and non-ferrous metals in packaging or during storage in closed rooms.

Zhang and Zhu (144) investigated N, N-Bis (4-morpholinyl methyl) urea was prepared from urea and N-hydroxymethyl morpholine and characterized by IR and 1 H-NMR. This compound was an excellent vapour phase corrosion inhibitor for ferrous metals and non-ferrous metals such as Cu, AI etc. Saturated vapour pressure of the inhibitor determined by knudsen method was 1.73 x 10-2 Pa at 23°C. Electrochemical polarization curve showed that compound inhibited cathodic process of metals.

Skinner et al. (145) evaluated five vapour phase corrosion inhibitors (VCIs) for their inhibition characteristics with multimetals. The minimum dosage required for mild steel protection, the influence of sulphur dioxide contamination and durability were also investigated. Of the relatively new inhibitors, diethylammonia caprylate performed the best.

Zhang and Zhu (146) evaluated the property of HA1 vapour phase inhibitor. It showed that HA1 has better protection for steel, copper and aluminium, compared with dicyclohexyl amine nitrite. Its inhibition mechanism was studied by simulated atmospheric corrosion electrochemical technique. The results showed that it had inhibition effect for both anodic and cathodic electrochemical process of steel.

Subramanian et al. (147) studied atmospheric corrosion of mild steel, copper and zinc in SO_2 environment under dynamic flow conditions by weight loss measurement, and their corrosion prevention by the use of volatile corrosion

inhibitors such as cyclohexylamine (CHA) and dicyclohexylamine (DCHA) is discussed. These studies assume importance as S02 is one of the dominant pollutants in the atmosphere and more so in industrial belts affecting the stability of metal articles to a greater extent.

Rajagopalan et al. (148) examined the performance of m-dinitrobenzene and β-naphthol as vapour phase inhibitors has been investigated at different humidities, and in presence and absence of sulphur dioxide and sodium chloride employing test specimens of mild steel and copper, zinc and aluminium. The two inhibitors give satisfactory protection to steel under a variety of experimental conditions and do not have an adverse effect on the non-ferrous metals.

Benzimidazole, 2-benzimidazolethial, benzotriazale and mercaptobenzotriazole are reported to be effective for Cu, AI, Zn and their alloys (149).

Reaction products of methyl benzotriazole with water soluble guanidine class compounds such as guanidine carbonate or nitrate or methyl, dimethyl, trimethyl, ethyl or diethyl guanidine in a molar ratio of 1 :0.5-1:2 were found to be effective atmospheric corrosion inhibitors for Cu, brass, Sn, tin plated steel and AI (150).

Products obtained by reaction of benzotriazole, ethylbenzotriazole and methyl benotriazole with soluble urea compounds e.g. urea, methyl, ethyl, propyl or dimethyl urea in molar ratio of 1 :0.5-1:2 at 10°-60°C were found to be effective for Cu, steel, AI and Zn (151).

The reaction product of benzotriazole with polyamine e.g. ethylenediamine and carboxylic acid and dissolved in spindle oil, effectively resists atmospheric corrosion of Fe, Cu, AI and Zn (152).

1.11 MECHANISM OF VAPOUR PHASE CORROSION INHIBITORS (VCIs)

It is widely accepted that the vapour phase inhibitors function by getting adsorbed on to the metal surface and thus forming a protective layer that limits penetration of the corroding species (153). This mechanism is graphically in following Fig, in which two functional groups are attached to the nucleus R:R*, which is responsible for the adsorption of the inhibitor of the metal surface and R** which gives thickness and impenetrable nature to the protective inhibitor layer.

Figure: Mechanism of corrosion inhibitor.

A VCI reaches the surfaces that it must protect from through the vapour phase. This transport mechanism requires the VCI to have an optimum vapour pressure. If the vapour pressure of VCI is too low, the protective vapour concentration will be established only slowly. If the vapour pressure of the VCI is too high, its effectiveness will be limited to a short time as its consumption rate will be high. For These reasons, VCIs having 'optimum' volatility are required for any given situation.

In the presence of moisture, the VCI molecule becomes polarized and is attracted to both anodes and cathodes on the metal. Once the VCI protective ions have adsorbed onto the surface, electrochemical process of corrosion is interrupted as the ions create a protective barrier to contaminants such as oxygen, water, chlorides, and other corrosion accelerators. With the protective barrier in place, the corrosion cell can not form and corrosion is halted. That barrier self-replenishes through further condensation of the vapour (70).

Electrochemical behaviour investigations show that VCIs compounds belong to mixed or "ambiodic" inhibitors capable of slowing both cathodic and anodic corrosion processes. The reduction of the cathodic reaction results from a diffusion in oxygen concentration caused by the formation of an adsorbed film that acts as a diffusion barrier for oxygen. Strong inhibition of the anodic reaction results from the

inhibitor's two acceptor-donor adsorption centers that form a chemical bond between the metal and inhibitor. Adsorption of mixed VCI compounds changes the energy state of metallic ions on the surface, diminishing the tendency of metal to ionize and dissolve (154).

E. M. Agres (155) studied the elucidation of the mechanism of the slowest stage of transport of a volatile inhibitor from the vapourization surface to the metal surface.

Rosenfeld et al. (156) described the transport mechanism for di(cyclohexyl) amine nitrite involves vaporization of the inhibitor in a non-dissociated molecular form, followed by hydrolysis on the metal surface.

Rosenfeld et al. (157) recorded the anodic and cathodic polarization curves of electrodes covered by a thin (approximately 100 micrometers thick) electrolyte layer during his study of inhibitors at the metal-solution interface and their effect on the corrosion processes. In this work, he demonstrated that inhibition can not be correlated to the alkalization process alone and that inhibition is usually due to the appropriate adsorbed organic cations on the metal surface.

Romanita (158) reviewed the mechanism of action of organic N-compounds, esters, amines, carbanimates and thiourea derivates as VCI for metals.

In all the cases, it has been suggested that adsorption of vapours of compounds play an important role for inhibition followed by secondary process e.g. reduction of molecules on the metal surface and thus exceeding critical current demities required for the passivation of metals.

Some other reviews (159-161) dealing with the mechanism of action of atmospheric inhibitors also deserve attention.

1.12 MEASUREMENT OF VAPOUR PRESSURE OF VCIs

At some temperatures and pressure, a solid or liquid is in equilibrium with its vapour. This equilibrium pressure is called the vapour pressure of the solid or liquid. Selection of a suitable inhibitor for a particular metal and environment depends upon the vapour pressure of compounds. Vapour pressures of dicyclohexylamine nitrite and cyclohexylamine carbonate e.g. are 0.0002 and 0.04 mmHg respectively at 25

^{0}C and both are effective for steel, Al and tin plate. The later compound exerts 2000 times higher vapour pressure than former inhibitor and therefore it is advisable to use it in system where the pack is opened frequently as its vapour saturates the container quickly. Measurement of vapour pressure, therefore plays an important role in developing the inhibitors for various systems.

Knudsen effusion method (162) was used to determine saturated vapour pressure of inhibitors and their temperature dependence, it consists of measuring the rate of gas effusion through a small orifice. The vapour pressure of inhibitor, depending on temperature, can satisfactorily conform the straight line in log P Vs 1/T coordinate system. This makes it possible to calculate the latent heat of sublimation by clapeyron-clausius equation.

Andreev et al. (163) analysed the possibility of calculating of the vapour pressure of of the salt type volatile inhibitors. It found that organic salt of the onium type sublimate in accordance with the dissociative mechanism; hence the saturated vapour pressure can be estimated from the constants of ionization of acid and base the salt is composed of, their volatility and solubility, and the solubity of the salt itself.

Andreev (164) studied vapour pressure of VCIs based on the free energy linearity principle and on the scale of $E_\xi R$ constants, which reflect the contribution of an R substituent to the free energy of vaporization of organic compound, an approach for predicting the vapour pressure of volatile organic inhibitors is analysed.

Rozenfeld et al. (165) investigated a gas adsorption method was used to determine the latent heat of sublimation of hexamethyleneimine benzoate and number of hexamethyleneimine m-benzoate molecules adsorbed per square centimeter of iron and nickel powders. The method make it possible to study the adsorption of inhibitors at extremely low degrees of surface coverage and also to determine the vapour pressures and heats of sublimation of volatile corrosion inhibitors.

One of the most convenient static methods is isoteniscope. This was used to determine the vapour perssure of liquids (166).

For solids, vapour pressure measurements were carried out by the Regnault dynamic

method (167). A weighed amount of inhibitor was heated at constant temperature in a slow stream of oxygen free nitrogen gas and the loss in weight was measured. Barometric pressure were recorded to reduce the volume of nitrogen to 760 mm pressure. The temperature range was from 2SoC to 60°C. The rate of volatilization of the compound at various temperatures was obtained.

$$\frac{\text{Total volume of compound}}{\text{Volume of the vapour}} = \frac{\text{Total pressure vapour}}{\text{Vapour}}$$

Thus, a vapour pressure temperature curve was obtained, which was used to predict the vapour perssure of the compound. The accuracy of the method was subject to the position of temperature control and barometric pressure measurements.

The vapour pressure measured using microbalance by following loss in weight at controlled temperature after due calibration with compounds of known vapour pressure (168).

Subhash et al. (169) calculated a set of 379 molecular descriptors for use in hierarchical quantitative structure-property relationship (QSPR) modeling of vapour pressure for a structurally diverse database consisting of 469 chemicals.

1.13 EVALUATION OF VCIs

The International standardization Organization (ISO) technical committee "Corrosion of Metals and Alloys" was active in developing standards for atmospheric corrosion testing and atmospheric corrosivity classification. An approach to define these standards and the use of information on corrosivity of the atmosphere for selection of materials and protective measures (170).

Romanov and Khanovich (171) evaluated the effectiveness of VC Is in terms of the following parameters

(i) time of inhibitor loss

(ii) relative loss of inhibitor

(iii) time of appearance of first corrosion products

(iv) relative residual quantity of inhibitor when corrosion starts.

(v) rate of corrosion and

(vi) factor that allows for the nature of corrosion.

Various accelerated corrosion test were in use. Before using any of these tests, one must exercise caution (70). Experimental results of accelerated tests in which artificially increased concentration of corrosive agents, e.g. SO_2, H_2S or NaCI were used should be compared to actual field performance only after proper calibrations. This warning was also expressed by Rosenfeld et al (172) explaining that reproducibility of datadepends upon experiment parameters that are inherent properties of the test method employed.

A widely used evaluating method to describe the relative abilities of inhibitors to prevent rusting of steel is described under ASTM D 1448 'Rust Protection by Metal Preservatives in the Humidity cabinet'. The summary of this method is stated as follows steel panels are prepared to a prescribed surface finish, dipped in the test oil, allowed to drain and then suspended in a humidity cabinet at 48.90 ± 1.1^0C(120 ± 2°F) for a specified number of hours. The oil fails or passes the test according to the size and number of rust dots on the test surfaces of panels. An essentially identical test method is described under Federal Test Method standard No. 7918, Method 5329.1. Corrosion Protection (Humidity cabinet).

Recently Andreev et al. (173) proposed the ways of enhancing the vapour phase protection. It is found that the effectiveness of a VCI in incompletely sealed systems can be estimated in accelerated tests by decreasing its dosage and increasing the mass exchange surface since these factors stimulate corrosion without violating the similarity principle.

Pucie et al. (174) used Particle induced X- ray emission (PIXE) spectroscopy for the determination of volatile corrosion inhibitor concentration in anticorrosion polymer films. PIXE spectroscopy of anti-corrosion polymer films revealed significant concentration of molybdenum implying that corrosion inhibitor was molybdate based. The films were divided into three groups according to different rate of the VCI concentration decrease with increasing age.

Volatile corrosion inhibitors (VCIs) are incorporated into packaging paper or film to protect metals against atmospheric corrosion. The vapour pressure determines the equilibrium concentration of a volatile corrosion inhibitor (VCI) in the surrounding atmosphere. However, the rate at which the VCI can delivered across the air gap to a metal surface is determined by the gas permeability. This gas permeability of commercial VCIs was estimated at elevated temperatures from vaporization rates measured using a simple thermo-gravimetric method (175).

Tormoen et al. (176) studied the adsorption of volatile corrosion inhibitors (VCIs) in-situ and in real time using surface-enhanced Raman spectroscopy (SERS). Two commercially available VCI emitter products were evaluated, and the effect of humidity on adsorption kinectics were examined. Significant differences in the adsorption kinectics were noted between the products. It was shown that the adsorption of VCI did not occur below a relative humidity of about 20%.

A systematic research on a modified method that was devcloped by Wan Hong-jing (177) to evaluate the effectiveness of volatile corrosion inhibitor (VCI) materials was carried out. The metal specimen in size of 50 mm × 25 mm × 2 mm was level mounted on the top of beaker by transparent adhesive tape and the assembly was placed in a constant temperature water bath and kept at approximately 40 ^{0}C to accelerate the vaporization of VCI and distilled water, which was placed at bottom of the beaker at the same time. The experimental results show that the reproducibility of rust appearance and corrosion rate calculated by specimen's mass loss is perfect. The outstanding characteristic of the rust appearance based on different VCI formula discovered that is very important in studying the mechanism of VCI and synergism of chemical reagent. The accelerated ratio is increases greatly as compared with the traditional method and the value is 15 as compared with Shijiazhuang atmospheric environment corrosion test. The modified method is suitable for formula screening test and quick effectiveness evaluation of VCI materials.

Furman (178) evaluated corrosion protection provided by VCIs vs. distance from its sources by corrosion monitoring, utilizing metal coupons and Corrosometer with special probs.

K L Vasanth (179) studied the reliability of thin film inductive magnetic recording heads under exposure to an elevated temperature and high humidity condition with and without saturated NaCl solution in the absence of a VCI emitter, and again in presence of a VCI emitter. In the process all heads were characterized by spin stand tests and chemical composition of heads was analysed before and after the exposure using a JEOL 8900 Electron Prob Microanalyser with a Noran thin window Electron Dispersion Spectroscopy (EDS) Detector.

A simple four point probe design using two Cu-wire to monitor the efficiency of a volatile corrosion inhibitor (VCI) is described by Jalger et al (180). Testing consisted of an aggressive atmosphere containing H_2S and relative humidity 80% to accelerate the corrosion process. The unprotected samples showed a greater voltage increase than the inhibited samples. Comparing the two rates identifies a higher corrosion rate for the unprotected sample and identifies on inhibitor efficacy for the inhibited samples. In addition, SEM images revealed different surface changes in the oxide for the Cu surfaces.

Furman and Chandler (181) studied the protective properties of vapour corrosion inhibitors are directly related to their ability to adsorb on the metal surface, the adsorption process is used to evaluate their performance. Their effectiveness is measured by various military. specifications and Federal Standards. Testing procedures developed by Cortec Corp. for evaluating their performance include F-12 cycling corrosion test, SO_2 test procedure and razor blade test.

Zhou Halhi et al. (182) studied the inhibition performance of several VCIs for carbon steel (0.45% C), 18-8 stainless-steel and H-62 brass was examined. Based on analysis of E- T attenuation curves, relevant parameters R_p, C_j, R_f and C_f in equivalent circuit for the electrode system were obtained, thus the inhibitors could be evaluated quickly. the results from the static coulometric method were consistent with those from weight loss testing.

Fujita Toshio (183) examined the quality, efficiency, testing methods of water and oil soluble volatile corrosion inhibitors (VCIs) and the effect of inhibitors on plastics.

Lea (184) used to detect and determine the depth-distribution of trace quantities of

boron in the surface layer of an iron-chromium steel such a technique can obviously to expanded to many other inhibitor system. The use of another analytical method, electron spectroscopy for chemical analysis (ESCA), with its unique capabilities for surface analysis also offers promise for these investigations. ESCA probes only the top 30 to 50 AD of a surface but it provides elemental analysis and chemical bonding information, it is also a non-destructive method that analysis any solid surface. It is sensitive to all elements except hydrogen.

A number of other methods have also been used for the investigation and evaluation of VCIs. Measurement of the quantity of inhibitor adsorbed on the metal surface may be accomplish by the use of sufficiently sensitive microbalance (185).

Rosenfeld et al. (186) followed the degree of VCI-provided protection of metal specimen by measurement of changes in their chronic resistance.

Kar (187) used capacitance measurements in kinetic studies of electric double layer on the metal surface. Electrochemical methods for investigation of VCIs have been used by many researchers.

Auto radiography was used by Hendricksen (188) for the determination of surface distribution of VCIs. Hendricksen also showed that when metal surface were exposed to VCIs in closed containers, theywere covered by a hydrophobic adsorbed layer. He measured the contact angle of distilled water on these surfaces.

Schwabe et al. (189) used radiochemical methods to evaluate C-containing di(cyctohexyl)amine and its nitrite and dibenzylsulfoxide.

Polling (190) used infrared techniques to study VCI deposits. Yu Yao (191) used mass spectorscopy to study the effect of various amines as corrosion inhibitors or iron surfaces.

1.14 METHODS OF APPLICATION OF VCIs

VCIs are available in many different media, common formulations include oils and greases, points and coatings, plastic films and wrapping papers, powders, fluids and emitter/vaporise devices. Selection of the correct VCI delivery medium may be the single most important factor in the effectiveness of the method (192).

1.14.1 Powders

Protecting voids and enclosed spaces is always a problem. Painting these spaces is difficult. Surface preparation costs are high and results can be marginal if there are a lot of stiffener, welds and fittings. Applying a high-quality multi-coat paint system is almost impossible, final welding and fabrication destroys paint film at the weld a practical solution is to fabricate the assembly, then install VCI powder though access holes or fittings. If further weld is necessary on the shell of the old, the VCIs volatilize at the heated area, then re-deposit on cooling. VCI vapours penetrate crevices, lap welded joints, or blow holes in the weld itself.

The common use of VCI powder is void protection. Applications include interiors of pipe (as manufactured or as a fabricated assembly), sea-land containers, ships and box beams for bridges and dams.

VCI powder is used to protect process equipment such as heat exchangers, pumps, boilers, boiler tubing, reactors, oil and product storage tanks for months and years.

Being a powder, it is important that distribution be relatively uniform in equipment. Where there are complex internals, dead areas: multiple bends and interior baffles, careful consideration must be given to achieve good distribution. Powder particle size is important as is providing internal flow paths, opening flanges, values and possibly suction or fans to promote distribution.

1.14.2 Emittes/Vaporizers

The problem of protecting electrical and electronic components is another difficult task. Most components are manufactured with degree of corrosion protection, depending on many factors.

Vaporizers emitters, cuches or similar devices are used to provide corrosion protection over a broad range of conditions. Installation can be part of factory packaging or applied later. A blend of VCI powder is incorporated into foam or packaged in paper or plastic containers. These containers allow a controlled release of VCI vapours into an enclosed space over time. This delivery method eliminates dust or loose powder.

A closed space is necessary for the vapourizer to be effective. An electrical panel, control cabinet, or even packaging such as plastic bag or a cardboard box is sufficient. VCI molecules deposit on the metal, protecting delicate electronic and electrical circuits, finely machined surface, and deep crevices, even in aggressive atmospheres. The equipment typically can remain active while it is being protected. There is no need for removal of the VCts device other than to replace it at the end of its service life.

1.14.3 Liquid VCIs

Protection of highly ventilated electrical enclosures and fixtures is another difficult corrosion problem. Moisture and corrosive gases slowly attack painted and unpainted surfaces. Protective of small parts (or large, unpainted machined surfaces) from corrosion, including nuts, bolts, hinges, motor shafts, coupling and mechanical seals, is a problem because many parts can not be painted.

For electrical applications, the combination of a emitter/Vapourizer and a liquid VCI electrical spray gives excellent protection even with ventilation or frequent opening of the container. This spray contains contact inhibitors and VCIs that vapourize quickly, providing almost instantaneous protection.

1.14.4 Temporary Inhibitor Coatings (TICs)

TICs are an ideal answer when surface protection is needed and paint is not really the answer. Painted equipment still has bars metal, sharp edges, hinges, hydraulic cylinder rams, plated parts and other surfaces that may suffer from corrosion overtime. TICs (clear, translucent or tinted) can be applied over most surfaces and are easily removed (not always necessary) just prior to use.

VCIs and contact inhibitors are incorporated into oils, water-based resins and other careers to produce these TLCs. These inhibitor films provide very effective protective properties at low film thickness (0.5mil to 5 mil). They can withstand months and years of outside exposure.

Several have the ability to be applied over salt-rusted steel, totally stopping corrosion activity for months or years. Many of these films are softer and normal paint and this must be taken into account.

1.14.5 VCI Polyethylene and Paper

VCI plastic films and papers are used when normal packaging does not work and vacuum or desiccant packaging is too expensive, difficult or still fails from the rigars of the real world.

Incorporation of VCIs into the packaging reduces chances for corrosion to start. Complex machinery has many components that are susceptible to corrosive attack. Spar parts are packaged in VCI paper, VCI plastic such as stretch or shrink film, VCI Ziplock bags or dipped in VCIs prior to packaging. VCIs pallet covers protect skids of parts or equipment quickly and economically. Corrosion damage is minimized, at low cost.

1.15 APPLICATION OF VCIs

The efficacy, convenience, and cost effectiveness of vapour phase corrosion inhibitors (VCIs) packaging products have made their application for rust control almost universal in automotive, machine tools, aerospace, electronics, power generation, and the military.

The VCIs technology protects metals from corrosion during manufacture, process, shipment, and storage (193).

Volatile corrosion inhibitors were originally developed to protect boilers and piping systems of ships to be mothballed. Their effectiveness and ease of application attracted early users. Over the years, the field of usage has increased to cover electronics, packaging, process industries, reinforced concrete, coatings, and metalworking fluids (194).

Corrosion damages billions of dollars of military assets every year. The application of vapour phase corrosion inhibitor products and systems used successfully by military organization worldwide (195)..

Corrosion is a problem faced by fire sprinkler industry in both wet and dry sprinkler system piping. VCIs provide protection in conditioned present in wet and dry pipe systems (195).

Incorporating of VCIs in lubricating products provide number of advantages. VCis when added to lubricant will provide corrosion protection to machinery during storage or transportation period (196).

Vapour phase corrosion inhibitors used for the protection of the aging aircraft (197), steel in concrete (198), metal surfaces in electrostatic field (199) and naval vessels (200).

1.16 CORROSION INHIBITION BY COOLING WATER INHIBITORS

Process industries require enormous amounts of water to provide necessary heat reduction at various stages of manufacturing process. This heat reduction is carried out in cooling water systems. Cooling water systems, intrinsic part of most of the industries, are broadly grouped into three types, viz., once through, open recirculating and closed recirculating systems. The characteristics of cooling water systems are as follows:

1.16.1. Once Through System

In the once through system cooling water passes through the heat transfer equipment only once before it is discarded as waste. The system is highly uneconomical as large amount of water is used and only a small temperature change occurs across the heat exchanger. However, the mineral content of water remains essentially the same. The application of once through systems is limited to areas with an abundant water source and to systems requiring marginal amounts of cooling water.

1.16.2 Open Recirculating System

The system water which is used to absorb heat from the hot process fluids heat transfer equipment is cooled by evaporation in a cooling tower or a spray pond and recycled again and again through cooling equipment. In cooling tower operations, the water cascade occurs. Make up water is added to compensate the evaporative losses. Due to scarcity of water resources open recirculating cooling water system is the most favoured system since it reduces water consumption by over 90%. As evaporation proceeds, the dissolved solids content of the water increases until solubility considerations necessitate its limitation (Le. by blowdown). Intimate

contact of the recirculating water with the atmosphere keeps the dissolved oxygen content of the recirculating water near saturation. Both of these factors - high content of dissolved solids and oxygen increases the corrosivety of water.

1.16.3 Closed Recirculating System

In this system, water recirculates in a closed cycle and is subjected to alternate cooling and heating without air contact. The heat absorbed from heat transfer equipment is dissipated into another heat sink, which is cooled by other methods. As there is no evaporation losses, the make up water requirement is minimal and the mineral content of the water remains essentially constant. Closed recirculating system is employed only in special circumstances. Successful cooling water treatment programs must control corrosion, scales and microbial fouling. All of these problems are interrelated and no one can be isolated from the other.

1.17 COOLING WATER TREATMENT

Treating the cooling water system with chemical formulations to overcome corrosion, scaling and fouling, is very important for trouble free operation. Inhibitors, small additions, reduce the aggressiveness of the environment towards metal. The role of cooling water inhibitors in industries is to permit more extensive use of iron and carbon or low alloy steel by protecting them from the corrosive medium, while at the same time reducing the maintenance/inspection and the frequency of shutdowns. This is generally more attractive in open or closed recirculating systems. Since different metals are used throughout the network of the system, metal picked up in one area can result in deposition and the setting up of galvanic couples in another. Inhibition in cooling circuits requires more than the simple addition of inhibitors; the conditions must be favourable for the inhibitor to work effectively

Numerous chromates (201,202), zinc (203,204), nitrites (205,206), molybdates (207), phosphonates (208-211), gluconates (212,213), polmers (214-218), multicomponent systems (219-224), amines (225-228) have been used as corrosion inhibitors for cooling water systems.

1.17.1 Corrosion Inhibition by Natural Compounds

It has been reported in the history of corrosion inhibitor that certain plant extracts brought about the suppression of the dissolution reaction of the metal dipped in different corrosive environment (229). As an example, tannins and their derivatives have been used since old times to protect steel and iron tools and pipelines (230). The extracts of some common plants and by products contain different organic compounds and were found quite effective in retarding the dissolution of steel in HCI and NaOH medium (231).

The effects of aqueous extracts of fenugreek lupine, Doum, cerum petroselinum, opentia ficus indica, pomegranate fruit shells solanum melongena, orange peels and Ammi majus as inhibitors for both corrosion and scale formation have been investigated (232). Most of the extracts of above plant materials were effective in retarding corrosion and scales.

The extracts of curcumin and agaricus were found quite effective in preventing the corrosion of mild steel in neutral aqueous medium (233,234).

Rajendran et al. (235) used an aqueous extract of the plant material rhizome(Curcuma longa L.) powder as a corrosion inhibitors in controlling corrosion of carbon steel immersed in an aqueous solution containing 60 ppm of Cl^- by mass-loss method in absence and presence of Zn^{2+}. The main constituent of this plant extract is curcumin. It has good inhibition efficiency.

Rehan (236) investigated water extract from leaves of date palm, phonix dactylifera, henna, lawsonia inermis, and zea mays were tested as corrosion inhibitors for steel, aluminum, copper and brass in acid chloride and sodium hydroxide solutions using weight loss, solution analysis and potential measurements.The inhibition action was found to critically depend on metal type and solution composition.

Al-Sehaibani (237) evaluated water extract of henna, lawsonia inermis, leaves powder as corrosion inhibitors for steel and commercial aluminum in saline, acidic and alkanine water.The maximum inhibition efficiency reported in this study was for extracts of 20 g of powdered henna leaves per litre.

Kliskie et al. (238) investigated the first neutral phenol subfraction of aqueous extract of rosemary leaves as corrosion inhibitors for Al-2.5Mg alloy in 3% NaCl solution at 25^0C. Experiments were carried out over a wide range of concentrations. The results show that the additives adsorb on alloy according to freundlich isotherm. The polarization curves show that the first neutral subfraction acts as a cathodic type inhibitors.

Barkat et al. (239) studied the corrosion inhibition of mild steel by some naturally occurring substance was evaluated in absence and presence of 600 and 1200 mg H_2S/l in 3% NaCl solution and pH of 3 and temperature of 25^0C. These naturally occurring substance included the water extracts, coumarines and fatty matters extracts of some Egyptian plants.

El-Etre (240) studied the inhibition action of natural honey on the corrosion of copper in a 0.5 M sodium chloride solution evaluated by using weight loss measurements and cathodic polarization technique. A good inhibition efficiency is observed which increase with an increase in inhibitor concentration.The Tafel,slope is changed markedly in the presence of natural honey.

1.17.2 Cooling Water Inhibitors for Brass

When a pure metal is immersed in a corrosive medium usually uniform dissolution of metal is observed. However, in case of brass (containing more than 15% Zn) preferential dissolution of zinc occurs. This special type of corrosion phenomenon wherein zinc is preferentially removed from the alloy leaving behind the spongy mass of copper with no mechanical strength is known as dezincification or dealloying. Dezincification can be of two types, viz., layer type and plug type. Inlayer type, dezincification proceeds uniformly over the surface. The surface appears to be covered with a tarnish layer but the bulk of the alloy does not have any strength. In plug type, dezincification leads to more rapid failure as it is localized in nature and proceeds with greater speed. This type of attack penetrates deep into the metal, forming porous plugs of copper but the entire surface is not affected. The mechanism of dezincification may be Preferential dissolution of zinc from the alloy Simultaneous dissolution of both zinc and copper followed by redeposition of copper. Both the above processes may occur under different circumstances.

Brass has been widely used as components in heat exchangers, pumps and in various industries. The alpha brass supplied for potentially corrosive environment contains arsenic to inhibit dezincification. Practical problems with dezincification are experienced with alpha - beta brass, used for example, for tube plates in old condensers or heat exchangers, for pipefitting or as vale components. Arsenic does not inhibit dezincification of alpha - beta brass (241). Studies on corrosion phenomenon of arsenic free alpha - beta brasses assume great significance, as they are susceptible to dezincification process.

Kurtz (242) studied fuel system assemblies used on recreational watercraft failed after a short time in service in a sea water environment. The source of the zinc chloride was established as corrosion products that resulted during the dezincification of internal brass connector through exposure to salt water in the application.

Santos et al. (243) studied the corrosion of brass in artificial sea water (ASW), and in neutral sea water (NSW). The weight gains and the corresponding average corrosion rates of brass samples immersed in both media, during periods of 1,3 and 6 months were determined. The concentration of Cu^{2+} and Zn^{2+} ions in solution, produced by the corrosion of brass, were determined by atomic absorption spectroscopy.

Zhdan et al. (244) studied corrosion at nano-thickness level is significant in the heat exchangers of power stations because of the subsequent transport of released copper throughout the steam/water circuit. One the most significant factors determining the extent of corrosion is the level of dissolved oxygen. In the work to be described, sample of admiralty brass have been exposed to pure water at 95^0C at different oxygen levels.

Many organic compounds have been used as corrosion inhibitors for brass in different media. Of these azoles have shown greatest efficiency (245,246). Recently emphasis has shifted to the use of organic compounds containing one or more polar atoms, e.g., nitrogen, sulfur, oxygen and compounds containing it π- bond, which affords excellent protection against corrosion of metals (247,248). Hackerman and Makrides (249) showed that sulfur containing organic compounds have special

efficiency, as these compounds are better electron donors than compounds containing oxygen and nitrogen.

Martinez et al. (250) studied a comparison of the corrosion of resistance of a bare Cu-10 Ni alloy and a Cu-10 Ni alloy protected by sodium-diethyl-dithiocarbamate ($NaEt_2dtc$). The experimental conditions varied from quiescent natural sea water to sea water subjected to jet impingement of different fluid velocities. The mechanism of inhibitor action has been suggested that includes the formation of a surface chelate compound between the dissolving metal ion and the $(Et_2dtc)^-$ ligand, as well as formation of a 3-D ternary surface complex.

Otmaeie et al. (251) investigated the efficiency of 1-phenyl-4-methylimidazoline for corrosion inhibition of copper in 3% NaCl solution. The formation of a thick layer on copper surface was observed in the presence of compound. The protective propertirs of this layer were characterized by means of cyclic voltametry and through AFM and SEM/EDX measurements.

Ekilik et al (252) studied the effects of the concentration and nature of acridine derivatives on the pseudoselective and anodic dissolution of β-brass, also with unstable surface morphology for different potentials. The effects of the inhibitors on mass transfer in liquid and solid phases were compared for the process controlled by both diffusion and kinetics.

Berchmans et al. (253) investigated the influence of a newly synthesized organic compound, 1,2,4,5 tetrazo spiro (5,4) decane-3 thione on the inhibition of corrosion of arsenical aluminum brass in NaCl solution using weight loss measurements, potentiodynamic polarization studies. Polarization studies reveal that the inhibition of corrosion of arsenical aluminum brass in NaCl is under mixed control.

Karpagavalli et al. (254) investigated the inhibitive action of benzotriazole (BTA), triton X-100 and the combination of both BTA and triton X-100 on the corrosion of brass in 1% NaCl solution and sea water. Potentiodynamic polarization measurements, open circuit potential vs. time plots, potentiokinetics measurements and cyclic voltammograms were recorded.

Benzotriazole (BTA) and methyl benzotriazole (tolyltriazole) have been used, for many years, as the most effective inhibitors for copper and copper based alloys. They form protective layers on the metal surface, the structure and bonding of these films have been studied by many investigators (255,256). It has been further demonstrated that the protective action of triazoles decreased markedly when applied in the presence of iodide ion (257). However, the inhibition efficiency of tolyltriazole decreases in the presence of chlorine.

Tolyltriazole, TTA, reacts with halogen based oxidizing biocides, and gets consumed in the bulk cooling water. In order to maintain an adequate supply of TTA in the bulk cooling water and at metal surfaces, more TTA must ve be added to the system. This reaction also produces an additional demand on the oxidizing biocide and leads to higher use levels in order to meet the cooling water total biocide demand. A new halogen azole has been developed for protection of copper alloys in aqueous solution (258). This material provides excellent copper corrosion inhibition in the presence of halogen based oxidizing biocides and offers better protection at reduced concentration than tolyltriazole.

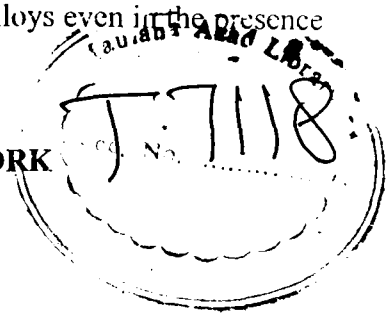
Zhang et. al. (259) studied the corrosion inhibition effect of benzothiazole and its derivatives on dezincification of brass in simulated cooling water by weight loss, atomic absorption and electrochemical techniques The inhibitive efficiencies of the inhibitors was found as: 2 - mercapto benzothiazole (2SH-BT) > 2 - amino benzothiazole ($2NH_2$-BT) > 2 methyl benzothiazole ($2CH_3$-BT) > benzothiazole (BT) The effect of sodium diethyl dithiocarbamate (NaDEDTC) on the corrosion of copper and brass in seawater has been evaluated by G.Latha et al. (260). NaDEDTC was found to prevent the corrosion of both copper and brass in seawater. The inhibitive action was attributed to metal sulphur bond formation. The addition of 100 ppm of. NaDEDTC for brass and 75 ppm of NaDEDTC for copper was sufficient to cause better inhibition.

The inhibitive action of some tetrazole derivatives on the copper corrosion in chloride solution has been studied by Zuchi, et.al. (261). Experiments have been carried out on copper corrosion in 0.1 M NaCI solution with the following tetrazole derivatives at 10-3 M concentration. Tetrazole (T), 5 - mercapto-1- methyl tetrazole

(5Mc-1Me -T), 5 mercapto(Na salt) -1-methyl tetrazole (5NaMc -1e-T), 5 - mercapto -1-acetc acid (Na salt) - tetrazole (5Mc - 1 Ac-T) , 5 - mercapto -1-phenyl-tetrazole (5Mc-1Ph -T), 5 - phenyl tetrazole (5Ph -T) and 5 amino tetrazole (5 NH2-T) in the pH range of 4-8 and at temperature of 40 - 80°C. Cathodic and anodic polarization curves were recorded after 1-hour immersion. All the inhibitors, except 5Mc - 1Ac-T, showed inhibition efficiencies from 50-99 %.5 Mc-1 Ph- T and 5 Ph - T exhibited better protective characteristics.

Processes of initial anodic selective dissolution of alpha brass in solutions containing sulphamic acid have been studied by Kaplan et al. (262). It has been shown that surface active quaternary ammonium salts exert protective action towards brass, due to their absorption on the metal surface, which changes the structure of double layer and increases the over voltage of the hydrogen evolution.

Three inhibitors, mercapto benzothiazole, benzotriazole, a tolyltriazole have been used for the protection of copper and based alloy (263). Benzotriazole and tolyltriazole control copper corrosion by reacting with the metal surface to produce a three-dimensional chemisorbed layer. The azoles are classified as cathodic inhibitors because they absorb at cathodic sites and interfere with the oxygen reduction reaction (264). Nitrite ion in combination with tolyltriazole was found effective corrosion inhibitor for copper and copper based alloys even in the presence of chlorine (265).



1.18 AIM AND OBJECTIVES OF THE PRESENT WORK

The aim of the present investigation was

(a) To synthesize some new hydrazide and its salts, schiff's bases and imidazoline salts as vapour phase corrosion inhibitors (VCIs) .

(b) To synthesize some new triazole derivatives as corrosion inhibitors.

(c) To investigate some natural products as cooling water inhibitors

(d) To study the inhibitive action of synthesized VCIs viz. hydrazide and its salts, schiff's bases, and imidazoline salts, on the corrosion of mild steel, brass, copper, aluminum and zinc in the vapour phase conditions.

(e) To study the inhibitive action of synthesized triazole derivatives on the corrosion of brass in NaCl water solution.

(f) To study inhibitive action of investigated natural products on the corrosion of mild steel in NaCl water solution.

(g) To investigate the mechanism of corrosion inhibition using potentiodynamic polarization technique.

(h) To study the influence of molecular structure on corrosion inhibition.

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Chapter-2

Experimental

2.1 MATERIALS

2.1.1 Test Specimen

2.1.1.1 For Weight Loss Method

Mild steel (0.14 % C, 0.35 % Mn, 0.17 % Si, 0..03 % P and Rest Fe), brass (70 % Zn and 30 % Cu), copper, aluminium and zinc of size 2.5 cm × 2.0 cm × 0.025 cm. were used for weight loss method. Specimens of size 5.0 by 2.0 by 0.025 cm. were used for Eschke test, Salt Inoculation test (Sodium Chloride Inoculation test) and SO_2 test.

2.1.1.2 For Electrochemical Method

Specimen having working area of 1 cm^2 and composition as above wre used foe all electrochemical tests.

2.1.2 Inhibitors Used

Inhibitors were synthesized in the laboratory. They are listed below

2.1.2.1 Hydrazide and Its Salts as VCIs

1.	Lauric Hydrazide	(LH)
2.	Lauric Hydrazide cinnamate	(LHC)
3.	Lauric Hydrazide nitrobenzoate	(LHNB)
4.	Lauric Hydrazide phthalate	(LHP)
5.	Lauric Hydrazide maleate	(LHM)
6.	Lauric Hydrazide succinate	(LHS)
7.	Benzoic Hydrazide	(BH)
8.	Benzoic Hydrazide benzoate	(BHB)
9.	Benzoic Hydrazide salicylate	(BHS)
10.	Benzoic Hydrazide nitrobenzoate	(BHN)

2.1.2.2 Schiff's Bases as VCIs

11.	Cinnamylidene lauric hydrazide	(CLH)
12.	Salicylidene lauric hydrazide	(SLH)
13.	Benzalidene benzoic hydrazide	(BBH)

14. Salicylidene benzoic hydrazide (SBH)
15. Cinnamalidene benzoic hydrazide (CBH)

2.1.2.3 Imidazoline Salts as VCIs

16. 1-(2-aminoethyl)-2-dec-9-enyl-2-imidazoline cinnamate (ADIC)
17. 1-(2-aminoethyl)-2-dec-9-enyl-2-imidazoline phthalate (ADIP)
18. 1-(2-aminoethyl)-2-dec-9-enyl-2-imidazoline nitrobenzoate (ADIN)
19. 1-(2-aminoethyl)-2-dec-9-enyl-2-imidazoline salicylate (ADIS)
20. 1-(2-aminoethyl)-2-undecyl-2-imidazoline cinnamate (AUIC)
21. 1-(2-aminoethyl)-2-undecyl-2-imidazoline phthalate (AUIP)
22. 1-(2-aminoethyl)-2-undecyl-2-imidazoline nitrobenzoate (AUIN)
23. 1-(2-aminoethyl)-2-undecyl-2-imidazoline cinnamate (AUIM)

2.1.2.4 Triazole Derivatives as Corrosion Inhibitors for Brass

24. 4-amino-3-butyl-5-mercapto 1,2,4 triazole (ABMT)
25. 4-amino-3-hydrazino-5-mercapto 1,2,4 triazole (AHMT)

2.1.2.5 Natural Products as Cooling Water Inhibitors for Mild Steel

26. Allium sativum (garllic) (AS)
27. Allium cepa (onion) (AC)
28. Ocimum basilicium (tulsi) (OS)

2.1.3 Synthesis of Hydrazide and Its Salts (Scheme-1)

2.1.3.1 Preparation of Hydrazide (1)

The fatty acids were esterified with methanol. A mixture of methyl esters of fatty acid (0.01M), hydrazine hydrate 99-100% (0.03M) and ethanol (25 ml) was refluxed for 8 hours. The solid that separated on cooling the concentrated reaction mixture was filtered, washed with little ethanol, then with ether and dried. It was then recrystallized from boiling water.

2.1.3.2 Preparation of Hydrazide Salts

Dissolving equimolar amount of hydrazide such as lauric hydrazide and benzoic hydrazide, and organic acid such as cinnamic acid, phthalic acid, nitrobenzoic acid,

maleic acid, succinic acid, benzoic acid and salicylic acid in ethanol. The reaction mixture was stirred for approx. one hour at 40 ^{0}C. The precipitated compound was filtered and crystallized from ethanol. Characterization data of the compounds are given below:

Compound No.	Name of the compound (Abbreviated)	Yield(%)	m.p (^{0}C)	R_f value Pet:E.A:MeOH (5:3:2)
1.	LH	95	85-86	0.37
2.	LHC	81	120-121	0.21
3.	LHNB	75	130-131	0.25
4.	LHP	78	135-136	0.28
5.	LHM	72	115-116	0.20
6.	LHS	79	140-142	0.19
7.	BH	90	80-81	0.45
8.	BHB	80	135-136	0.31
9.	BHS	72	122-123	0.26
10.	BHN	70	140-141	0.23

FT-IR Spectral data (significant bands ν_{max} in cm^{-1}(KBr))

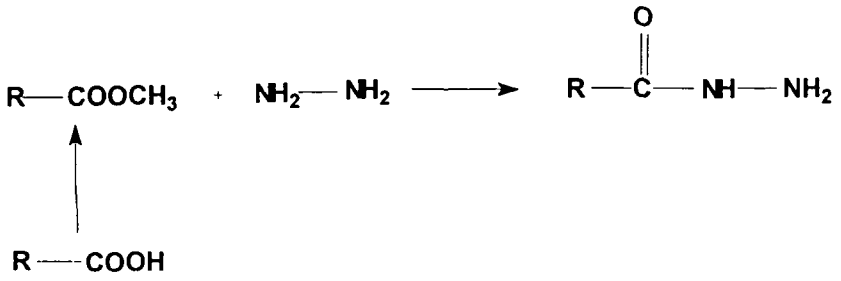
LH = 3300(N-N), 3250(N-H), 2900(CH_3), 2845(CH_2 chain), 1621(C=O), 1152(C-N)

BH = 1428(C_6H_5), 3312(N-N), 3250(N-H), 1621(C=O),1165(C-N)

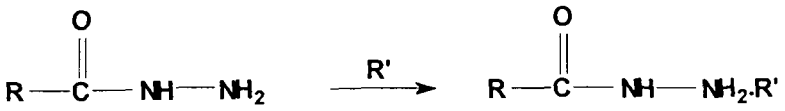
NMR Spectral data (δ $CDCl_3$)

LH = 1.36(16 H, $(CH_2)_8$), 2.76(2H, $C\underline{H}_2C$=O), 5.09(2H, $N\underline{H}_2$), 8.87(1H, N-$\underline{H}$), 0.9(3H, $C\underline{H}_3$)

BH = 7.53(1H,C_6H_5-$C\underline{H}$), 2.80(2H, $C\underline{H}_2C$=O), 5.02(2H, NH_2), 8.91(1H,N-$\underline{H}$)



1. R = CH_3-$(CH_2)_{10}$
7. R = C_6H_5



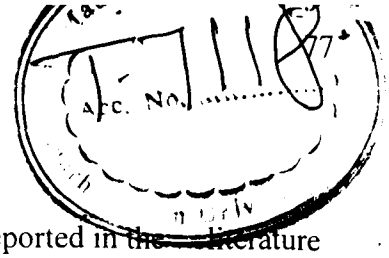
1. R = CH_3-$(CH_2)_{10}$

2. R' = C_6H_5-CH=CH-COOH
3. R' = $C_6H_4(NO_2)COOH$
4. R' = $C_6H_4(COOH)COOH$
5. R' = HOOC-CH=CH-COOH
6. R' = HOOC-CH_2-CH_2-COOH

7. R = C_6H_5

8. R' = C_6H_5COOH
9. R' = $C_6H_4(OH)COOH$
10. R' = $C_6H_4(NO_2)COOH$

Scheme-1



2.1.4 Synthesis of Schiff's Bases (Scheme-2)

Hydrazides were synthesized according to the procedure reported in the literature (1) as mentioned in the step-1 of scheme-1.

2.1.4.1 Preparation of Schiff's Base

Dissolving equimolar amount of hydrazide such as lauric hydrazide and aromatic aldehyde such as cinnmaldehyde, salicyldehyde, benzaldehyde in ethanol. The reaction mixture was stirred for one hour at 40^0C. The precipitated compound was filtered and crystallized from ethanol. The compounds with characterization data are given below

Compound No.	Name of the compound (Abbreviated)	Yield(%)	m.p (^{0}C)	R_f value Pet:E.A:MeOH (5:3:2)
11	CLH	70	80-81	0.55
12	SLH	65	95-96	0.48
13	BBH	68	168-169	0.45
14	SBH	65	148-149	0.30
15	CBH	60	139-140	0.38

FT-IR Spectral data (significant bands ν_{max} in cm^{-1}(KBr))

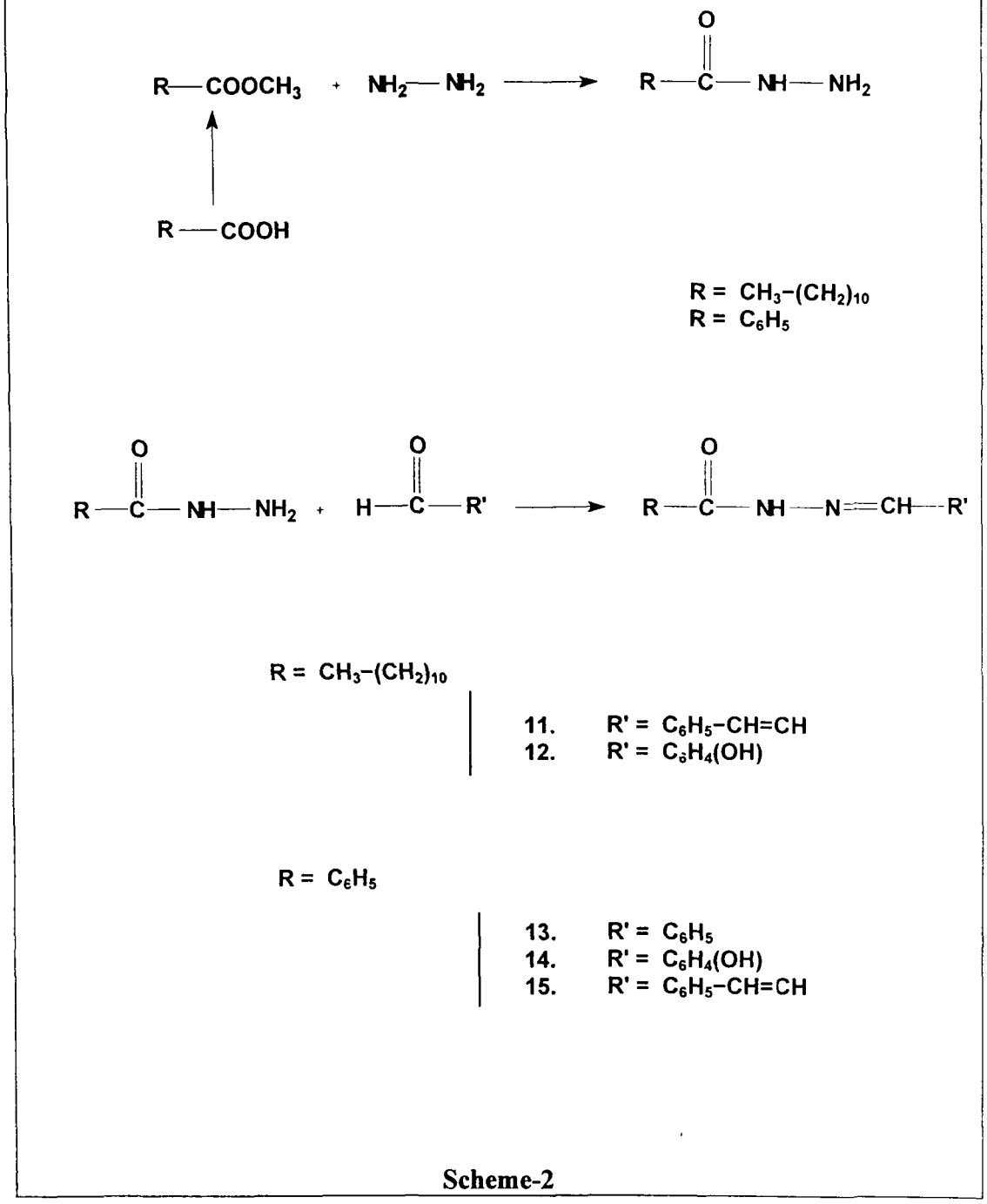
CLH = 3012(N-N), 3184(N-H), 2910(CH_3), 2848(CH_2 chain), 1710(C=O), 1280(C-N), 1431(C_6H_5), 1583(C=N), 1618(C=C)

BBH = 3014(N-N), 3250(N-H), 2910(CH_3), 1620(C=O), 1236(C-N), 1497(C_6H_5), 1631(C=N),

NMR Spectral data (δ $CDCl_3$)

LH = 1.70(16 H, $(CH_2)_8$), 2.76(2H, C<u>H</u>$_2$C=O), 8.80(1H, N-<u>H</u>), 1.0(3H, C<u>H</u>$_3$), 7.2(1H, C_6H_5CH=CH-C<u>H</u>)

BH = 7.59(1H,C_6H_5-C<u>H</u>), 2.72(2H, C<u>H</u>$_2$C=O), 8.96(1H,N-<u>H</u>), 7.73(1H, C_6H_5C<u>H</u>=)


R—COOCH3 + NH2—NH2 → R—C(=O)—NH—NH2
R—COOH
R = CH3–(CH2)10
R = C6H5
R—C(=O)—NH—NH2 + H—C(=O)—R' → R—C(=O)—NH—N=CH—R'
R = CH3–(CH2)10
11. R' = C6H5–CH=CH
12. R' = C6H4(OH)
R = C6H5
13. R' = C6H5
14. R' = C6H4(OH)
15. R' = C6H5–CH=CH

Scheme-2

2.1.5 Synthesis of Imidazoline Salts (Scheme-3)

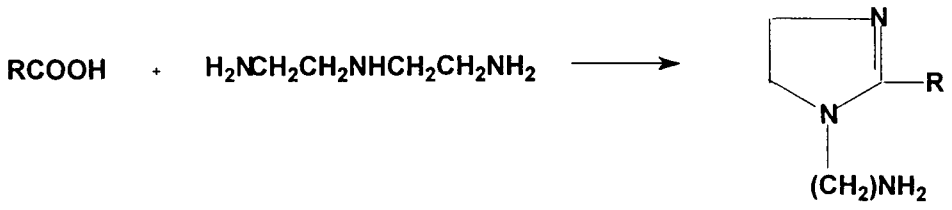
2.1.5.1 **Preparation of 2- Imidazoline** (2,3)

To 1.0 M fatty acid such as undecenoic acid and lauric acid, add 50 ml ethanol. Add 1.0 M thionyl chloride ($SOCl_2$) very slowly in cold. Reflux the reaction mixture for three hours. Add 1.0 M diethylenetriamine then reflux whole mixture for another three hours to get 2-imidazoline such as 1-(2-aminoethyl)-2-dec-9-enyl-2-imidazoline and 1-(2-aminoethyl)-2-undecyl-2-imidazoline.

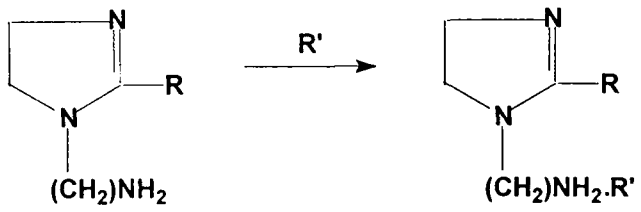
2.1.5.2 Preparation of 2-Imidazoline Salts

Dissolving equimolar 2-imidazoline such as 1-(2-aminoetthyl)-2-dec-9-enyl-2-imidazoline and 1-(2-aminoethyl)2-undecyl-2-imidazoline, and organic acid such as cinnamic acid, phthalic acid, nitrobenzoic acid, salycylic acid, and maleic acid in ethanol. The reaction mixture was stirred for one hour at 40^0 C. The precipitated compound was filtered and crystallized from ethanol. The compounds with characterization data are given below

Compound No.	Name of the compound (Abbreviated)	Yield(%)	m.p (^{0}C)	R_f value Pet:E.A:MeOH (5:3:2)
16	ADIC	63	62-63	0.28
17	ADIP	62	210-211	0.32
18	ADIN	58	140-141	0.36
19	ADIS	55	88-89	0.23
20	AUIC	68	115-116	0.38
21	AUIP	61	95-96	0.25
22	AUIN	59	90-91	0.30
23	AUIM	52	62-63	0.21



R = CH_2=CH–$(CH_2)_8$
R = CH_3–$(CH_2)_{10}$



R = CH_2=CH–$(CH_2)_8$

16. R' = C_6H_5–CH=CH–COOH
17. R' = C_6H_4(COOH)COOH
18. R' = $C_6H_4(NO_2)$COOH
19. R' = C_6H_4(OH)COOH

R = CH_3–$(CH_2)_{10}$

20. R' = C_6H_5–CH=CH–COOH
21. R' = C_6H_4(COOH)COOH
22. R' = $C_6H_4(NO_2)$COOH
23. R' = HOOC–CH=CH–COOH

Scheme-3

FT-IR Spectral data (significant bands ν_{max} in cm^{-1}(KBr))

ADIC = 3300(N-N), 2832(CH_2 chain), 1589(C=C), 1180(C-N),1688(C=N), 3178(N-H), 3200(O-H), 1711(C=O)

AUIC = 2980(CH_3), 2840 (CH_2 chain), 1042(C=N), 1268(C-N), 3200(N-H) 2930(O-H), 1720(C=O)

NMR Spectral data (δ $CDCl_3$)

ADIC = 1.30(12H, $(CH_2)_6$), 2.60(2H, $C\underline{H}_2$-CH=), 5.12(2H, $C\underline{H}_2$=CH), 0.9(3H, CH_3), 5.02(2H, $N\underline{H}_2$)), 5.96(1H, CH_2-CH-), 1.4(4H, $N(C\underline{H}_2)_2N$), 6.45(1H, = C<u>H</u>-COOH), 7.80 (1H, C_6H_5-C<u>H</u>), 7.53(5H, $C_6\underline{H}_5$) 11.80(1H, COO<u>H</u>)

AUIC = 1.40(16H, $(CH_2)_8$), 2.1(2H, CH_2-C), 1.1(3H, CH_3), 5.10(2H, $N\underline{H}_2$)), 1.4(4H, $N(C\underline{H}_2)_2N$), 6.45(1H, =C<u>H</u>-COOH), 7.80 (1H, C_6H_5-C<u>H</u>), 7.53(5H, $C_6\underline{H}_5$) ,11.80(1H, COO<u>H</u>)

2.1.6 Synthesis of Triazole Derivatives (Scheme-4)

2.1.6.1 Preparation of Thiocarbohydrazide (TCH) (4)

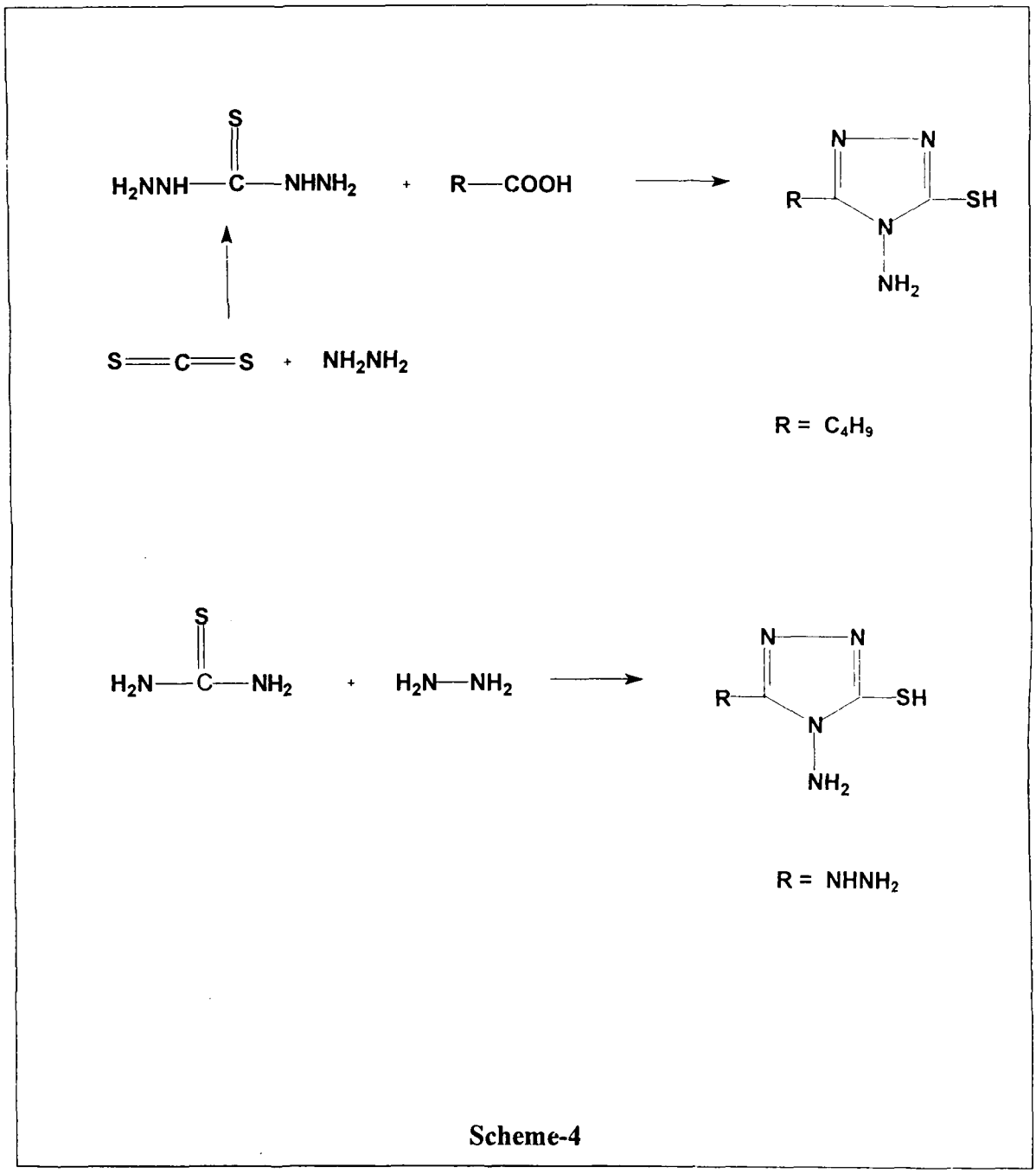
To a vigorously stirred solution of 250 g of 100% hydrazine hydrate (5.0 M) and 150 ml of water, add 76 g of 1.0 M carbon disulphide added dropwise. The reaction mixture was then heated at reflux for one hour. Cooled in ice bath for 30 minutes. The precipitated was filtered off, washed with ethanol and ether, air dried and crystallized from minimum quantity of water, acidified with few drop of conc. HCl

2.1.6.2 Preparation of 4-Amino-3-Butyl-5-Mercapto-1,2,4 Triazole (ABMT) (5)

A mixture of thiocarbohydrazide (10 g) and an acid (50 ml) in ethanol was heated under reflux for 3-4 hours.The reaction mixture was cooled to room temperature. The residual solid product thus obtained was crystallized from ethanol.

2.1.6.3 Preparation of 4-Amino-3-Hydrazino-5-Mercapto-1,2,4 Triazole (AHMT) (5)

A mixture of thiocarbohydrazide (10 g) and an hydrazine hydrate (100 ml) in ethanol was heated under reflux for 2-3 hours. The reaction mixture was cooled in ice and neutralized with dil. HCl , the preccipitated thus obtained was crystallized from ethanol.


S
H2NNH—C—NHNH2
+
R—COOH
N
N
R
SH
N
NH2
S═C═S
+
NH2NH2
R = C4H9
S
H2N—C—NH2
+
H2N—NH2
N
N
R
SH
N
NH2
R = NHNH2

Scheme-4

Characterization data of the compounds are given below

Compound No.	Name of the compound (Abbreviated)	Yield(%)	m.p (^{0}C)	R_f value Benzene: E.A (10:1)
24	ABMT	59	60-61	0.54
25	AHMT	63	75-76	0.46

FT-IR Spectral data (significant bands ν_{max} in cm^{-1}(KBr))

ABMT = 3200(N-H), 3110(N-N), 2940(CH_3), 2760(CH_2)
2560(S-H),1614(C=N), 1240(C-N),1093(C-S)

AHMT = 3200(N-H), 3110(N-N), 2940(CH_3), 2760(CH_2)
2565(S-H),1620(C=N), 1245(C-N),1105(C-S)

NMR Spectral data (δ $CDCl_3$)

ABMT = 5.12(1H, S-H), 5.07(2H, NH_2), 1.20(4H, $(CH_2)_2$),
2.10(2H, CH_2-C), 0.9(3H, CH_3)

AHMT = 5.10(1H, S-H), 5.09(2H, NH_2), 8.87(1H, N-H)

2.1.7 Natural Products as Inhibitors

In the present investigation many plant materials have been tried as inhibitors for mild steel. Out of the numerous compounds, the following compounds gained attention for the inhibition of mild steel surface.

Stock solutions of the inhibitors were prepared by extracting 50 g of dried and crushed materials in 500 ml of distilled water by boiling for one hour. The extracts were then filtered and concentrated to 50 ml. The extracts were then stored under refrigerated conditions (6).

The listed below gives the composition of the plant materials utilized as inhibitors for cooling water systems.

Compound No.	Name of the compound (Abbreviated)	Constituents
26	AS	Alliin, Allicin(diallylthiosulphinate), diallylsulphide
27	AC	Allyl propyl disulphide, flavonoids such as quercetin
28	OB	Caffieic acid, tannins, beta carosten

2.2 TECHNIQUES USED

2.2.1 Technique Used for the Characterization of the Synthesized Compounds

i. Determination of Melting Point

Melting points were recoded on Kofler hot block apparatus and are uncorrected.

ii. Determination of R_f values

R_f values were obtained by thin layer chromatography using Silica-Gel G_{254} (MERCK). Iodine was used for visualization of the TLC plates.

iii. FT-IR Spectroscopy

FTIR spectra were obtained in KBr with Spectrolab Interspec 2020 spectrometer. IRValues are given in cm^{-1}.

iv. Nuclear Magnetic Resonance

^1H- NMR spectra were run in $CDCl_3$ on a varian A-60 D spectrometer with TMS (Me_4Si). The chemical shift were recorded relative to TMS assigned at zero.

2.2.2 Techniques Used for Vapour Pressure Determination

i. Knudsen Method (7)

A standard Knudsen method was used to determine the vapour pressure of inhibitors. Weighed compound was placed in a glass container having orifice of 1.0 mm diameter. The glass container was placed in an oven at 40 ± 1^0 C for 20 days. Loss in mass was measured by an electronic sartorious balance and the values were put into formula given below:

$$P = \frac{W}{Axt} x \left(\frac{2\pi RT}{M}\right)^{1/2}$$

Where,

P = Vapour pressure of the inhibitor in Pascal (Pa)
(1 Pa = 752.47×10^{-5} mmHg)

A = area of the orifice in m^2

t = time of the exposure in seconds

W = weight of evaporated substance in kg

T = temperature in Kelvin

M = molecular mass of the compound in kg

R = gas constant (8.314 $JK^{-1}mol^{-1}$)

2.2.3 Techniques Used for Corrosion Study

i. Weight Loss Method

The specimen of required size of different steels were mechanically polished with 1/0 to 4/0 grade of emery papers. In each specimen a 1.5 mm diameter hole was drilled for mounting the specimen. After polishing, the specimen were washed with distilled water and degreased with trichloroethylene. The clear and dry specimens were measured for the total surface area using the following equation

$$A = 2(lb + lt - \pi r^2 + \pi rt)$$

Where,

t = thickness of the specimen in cm.

b = width of the specimen in cm.

l = length of the specimen in cm, and

r = radius of the mounting hole.

The weight of the specimen were measured before exposing it to the corrodent medium on a sartorious balance. The volume of test medium per square centimeter was maintained as per ASTM method, to avoid any appreciable change in its corrosivity during the test either through exhaustion of corrosive constituent or by accumulation of corrosion products that might effect further corrosion. The testing duration, medium/solution temperature and inhibitor concentration were varied with the purpose of the test, nature of test materials and apparatus used. The test conditions were controlled throughout the test in order to ensure reproducible results. After a definite exposure of time, the specimen was taken out and washed with running water. The corrosive product on metal surface, if any, was removed mechanically by rubbing with brush. The specimens were then dried and loss in weight was recorded. The percent inhibition efficiency (%I.E) was either calculated using following equation.

$$\% \text{ I.E} = \{(W^0 - W) / W^0\} \times 100$$

Where,

I.E = Inhibition efficiency

W^0 = Weight loss of metal in absence of inhibitor

W = Weight loss of metal in presence of inhibitor

The average corrosion rate was obtained by the use of the following equation

Corrosion Rate (CR) = K W / ATD

Where,

K = a constant (8.76×10^4 for mmpy)

W = weight loss in g

A = area in cm^2

T = time of exposure in hours, and

D = density in g / cm^3

Corrosion experiments were used carried out using ferrous and non-ferrous metals viz. mild steel, brass, copper, aluminum and zinc. The strips size 2.5 cm by 2.0 cm by 0.025 cm polished by emery paper of no. 1/0, 2/0, 3/0 and 4/0 were used for weight loss measurement studies. Weight loss experiments were carried out in the absence and presence of inhibitors at a fixed conc. 500 ppm using tight fitting rubber cork 250 ml conical flasks containing 25 ml water glycerine mixture (17.5 ml water and 7.5 ml glycerin) to produce 90% relative humidity. The concentration of inhibitors used for study was taken according to the volume of conical flask. The metal specimens were suspended in these flask by nylon tags and just below of these specimens weighed vapour phase corrosion inhibitors (VCIs) samples were kept in a glass container as not to be in contact with liquid inside the conical flasks. The conical flasks were kept in air thermostat set at temperature 40 ± 1^0 C. The experiment was conducted for 30 and 20 days. The metal coupons were placed in inhibited acid bath to remove corrosion products then weighed.

The percentage inhibition efficiency (%I.E) was calculated using following equation.

$$\% \text{ I.E} = \{W^0 - W / W^0\} \times 100$$

Where,

I.E = Inhibition efficiency

W^0 = Weight loss of metal in absence of inhibitor

W = Weight loss of metal in presence of inhibitor

ii. Eschke Test

Eschke test was carried out as per procedure in literature (8) using mild steel , brass and copper and aluminum. The strips size 5.0 cm by 2.0 cm by 0.025 cm polished by emery papers of no. 1/0, 2/0, 3/0 and 4/0 were used for Eschke test. The specimens were wrapped in single layer of inhibitor impregnated kraft papers and suspended in climate cabinet maintained at 90% relative humidity. One g/ft^2 of inhibitors were used for experiment. The temperature cycle was set at 40 ± 1^0 C for 12 hours and at room temperature for another 12 hours for condensation of moisture. The duration of test was 20 days. A similar experiment was done with metal covered with untreated kraft paper (control) i.e without inhibitor.

iii. Salt Inoculation Test (Sodium Chloride Inoculation Test)

Salt inoculation test was carried out as per procedure reported in literature (8) using mild steel, brass, copper and aluminum. The strips of size 5.0 cm by 2.0 cm by 0.025 cm polished by emery papers of no. 1/0, 2/0, 3/0 and 4/0 were used for salt inoculation test. The 0.1 g of sodium chloride was placed in 200 ml carbon tetrachloride and whole solution was stirred by magnetic stirrer. The metal specimen were introduced in stirred solution for 3-4 seconds and taken out when approximately 10-12 particles of salt were deposited at random on each side of the metal surface. The whole metal surface was wrapped in single layer of inhibitor impregnated kraft paper and suspended in climate cabinet maintained at 90% relative humidity. One g/ft^2 of inhibitors were used for experiment. The temperature cycle was set at 40 ± 1^0 C for 12 hours and at room temperature for another 12 hours for condensation of moisture. The duration of test was 20 days. A similar experiment was done with metal covered with untreated kraft paper (control) i.e without inhibitor.

iv. Sulfur dioxide (SO_2) Test

Sulfur dioxide (SO_2) test was carried out as per procedure reported in literature (8) using mild steel, brass, copper and aluminum. The strips of size 5.0 cm by 2.0 cm by 0.025 cm polished by emery papers of no. 1/0, 2/0, 3/0 and 4/0 were used for SO_2 test. The metal specimens were suspended inside one litre glass container. Weighed vapour phase corrosion inhibitor (VCI) was kept inside the container. A small beaker containing 0.04 g of sodium thiosulphate was placed inside the container. The 50 ml capacity beaker containing 30 ml aqueous solution of salt (1% NH_4Cl + 1% Na_2SO_4) was placed inside the container. The 0.5 ml of 1 N sulfuric acid was directly added to the beaker containing sodium thiosulphate and glass container was immediately sealed. The glass container was placed in a oven set at 40 ± 1^0 C for the duration of 16 hours and at room temperature for another 8 hours. A similar experiment was done with the one litre glass container in absence of VCI (control)

v. Potentiodynamic Polarization Technique

Working electrode 1.0 cm × 1.0 cm with a tag of 4.0 cm were cut from the metal sheet and polished with 1/0 to 4/0 grade of emery papers. The specimens were then thoroughly washed with distilled water and finally degreased with trichloroethylene. The unwanted area of the working electrode was coated with lacquer to get a well defined area of 1 cm^2. The polarization studied were carried out using EG & G PARC potentiostat / galvanostat (model 173), universal programmer (model 175), X-Y Recoder (model RE0089). A platinum foil and a saturated calomel electrode were used as auxiliary and reference electrode. All the experiments were carried out at a constant temperature of $28\pm2\ ^0C$ and at a scan rate 1 mV / sec. at OCP. The polarization curves were obtained after immersion of the electrode in the solution for 30 minutes until reaching steady state. The percentage inhibition efficiency was calculated using the following equation:

$$\% \text{ I.E} = \{(I^0_{corr} - I_{corr}) / I^0_{corr}\} \times 100$$

Where I^0_{corr} and I_{corr} corrosion current density without and with inhibitor respectively.

vi. Auger Electron Spectroscopy

Auger electron spectroscopy is one of the most popular and powerful technique to analyse the chemical species within the outermost surface layers of the specimen. The presence of different element species can distinguished by their characteristic peaks in auger spectra. The auger analysis of the samples was accomplished by using an electron spectroscope (Varian CMAVT-112). The beam energy of 3 keV was used to obtain the auger spectra. The depth of resolution was 2 A^0 to 20 A^0.

2.2.4 Technique Used for Solution Analysis for Dezincification

i. Atomic Absorption Spectroscopy

The concentration of zinc and copper in ppm were analysed with a atomic absorption spectrophotometer (Model GBC 902). The solution collected during the weight loss experiments.

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Chapter-3

Results and Discussion

Part – A

Corrosion Inhibition
by
Vapour-Phase Corrosion Inhibitors (VCIs)

Section – 1

Hydrazide and its Salts
as
Vapour-Phase Corrosion Inhibitors (VCIs)

Numerous investigations of corrosion inhibition have been utilized aliphatic amines, alicyclic amines, fatty acids, and their salts as vapour phase corrosion inhibitors for various industrial metals and alloys (1-5). Quraishi et al. (6-8) studied some organic volatile corrosion inhibitors for various metals and alloys.

In the present study the influence of some hydrazide and its salts as vapour phase corrosion inhibitors (VCIs) on corrosion of mild steel, brass, copper, aluminum and zinc under vapour phase conditions has been investigated by weight loss method, Eschke test, salt inoculation test, sulfur dioxide test, potentiodynamic polarization method and auger electron spectroscopy. The vapour pressure of the compounds was determined by Knudsen method.

3A.1.1 Corrosion Inhibitors

The molecular structure and other details of the compounds used as vapour phase corrosion inhibitors (VCIs) are given in Table 3.1.1 and Table 3.1.2 respectively.

3A.1.2 Vapour Pressure Determination

The values of vapour pressure of lauric hydrazide and its salts, and benzoic hydrazide and its salts, at $40\pm1^{0}C$ for 20 days obtained from Knudsen method are summarized in Table 3.1.3 and Table 3.1.4 .

3A.1.3 Weight Loss Studies

The various parameters such as percentage inhibition efficiency (%I.E) and corrosion rate (C.R) of different metals under vapour phase condition in absence and presence of lauic hydrazide and its salts at 1000 ppm concentration, and benzoic hydrazide and its salts at 500 ppm concentration, at $40\pm1\ ^{0}$ C and 90% relative humidity are summarized in Table 3.1.5 and Table 3.1.6 respectively. It has been observed from the results that all the compounds inhibit corrosion of mild steel, brass, copper, aluminum and zinc. The inhibition efficiency for all these compounds is found good at 1000 ppm of lauric hydrazide and its salts and at 500 ppm of benzoic hydrazide and its salts to give maximum efficiency.

The order of inhibition efficiency of examined VCIs has been found as follows:

LHC > LHNB > LHP > LHM > LHS >LH

BHB > BHS > BHN

The effectiveness of a given compounds as corrosion inhibitors depends on the structure of the organic compounds (9). The variation of inhibition efficiency mainly depends on the type and nature of the substituents present in the inhibitor (10). The corrosion inhibiting action of the VCIs is attributed to the presence of lone pair of electrons present on the N atoms of the inhibitor molecules, which facilitate adsorption for these inhibitors onto the metal surface.Thus on the basis of the above mentioned factors, the difference in protective action of VCIs can be explained.

The corrosion inhibiting effect of LH is attributed to the presence of a lone pair of electrons on the N atom of the molecule that facilitate adsorption of inhibitor molecules on the metal surface. In the present investigation, the LHC salt exhibited highest inhibition efficiency as a corrosion inhibitor owing to presence of an additional π bond between carbon atoms (-C=C-) which facilitates greater adsorption of cinnamate onto the metal surface. The corrosion inhibiting effect of the LHNB is attributed to the presence of a nitro group. The inhibitive action of LHP is attributed to the presence of an additional aromatic ring. The inhibiting effect of LHM is attributed to the presence of a double bond between the carbon atoms (-C=C-) through which they adsorb strongly onto the surface of metals. The inhibiting action of LHS is attributed to the presence of COOH groups.

The corrosion inhibiting effect of BH is attributed to the presence of a lone pair of electrons on the N atom of the molecule that facilitate adsorption of inhibitor molecules on the metal surface. BHB showed good inhibition efficiency due to the presence of extensively delocalized π electrons in benzene ring further facilitates the adsorption process. The inhibiting action of salicylate,BHS is attributed to the presence of OH group. The corrosion inhibiting effect of the BHN is attributed to the presence of a nitro group.

3A.1.4 Eschke Test

The results obtained by this test in absence(control) and presence of LHC and BHB at 40 ± 1^{0}C and 90% relative humidity for 20 days for various metals are given in

Table 3.1.7 and Table 3.1.8 respectively. The results show that minimum corrosion is taking place in presence of both LHC and BHB.

3A.1.5 Salt Inoculation Test

The results obtained when the metals are inoculated with sodium chloride in absence (control) and presence of LHC and BHB at 40±1^{0}C and 90% relative humidity for 20 days for various metals are shown in Table 3.1.9 and Table 3.1.10 respectively. The results show that number of nucleation is minimize in inhibiting metal coupons containing LHC and BHB.

3A.1.6 Sulfur dioxide (SO_2) Test

The results obtained by this test in absence(control) and presence of LHC and BHB at 40±1^{0}C and 90% relative humidity for 24 hours for various metals are shown in Table 3.1.11 and Table 3.1.12 respectively. It has been observed from the results that both the compounds LHC and BHB inhibit corrosion of various metals.

3A.1.7 Potentiodynamic Polarization Studies

The corrosion parameters such as corrosion current density(I_{corr}), corrosion potential (E_{corr}) and percentage of inhibition efficiency (%IE) obtained from the potentiodynamic polarization curves in absence and presence of lauic hydrazide and its salt, and benzoic hydrazide and its salts at 500 ppm concentration, at 28±2 ^{0} C are given in Table 3.1.13 and Table 3.1.14 .

Potentiodynamic polarization studies were carried out by immersing metal coupons and inhibited coupons in a 1 N Na_2SO_4 solution (11). The I_{corr} value was found to decrease significantly in presence of inhibitors, indicating that the compounds were effective corrosion inhibitors. All of these compounds shifted the E_{corr} in a more positive direction, suggesting that they were predominantly anodic inhibitors. Figures 3.1.1 A-E and figure 3.1.2 A-C show the Tafel plots obtained from different inhibited coupons in presence of the 1 N Na_2SO_4 solution for mild steel, brass, copper, aluminum and zinc.

Guo Gao et al. (12) studied some organic compounds tested as VCIs for brass in simulated atmospheric water using potentiodynamic polarization method. Polarization curves showed that the compounds acted as good anodic inhibitor.

3A.1.8 Auger Electron Spectroscopy

Figure 3.1.3 and figure 3.1.4 show auger electron spectra for mild steel and copper surface inhibited with 500 ppm of laric hyrdrazide cinnamate respectively. The appearance of peaks supports the adsorption of LHC through N and O atoms.

3A.1.9 Mechanism of Corrosion Inhibition

Inhibition of metallic corrosion in presence of lauric hydrazide salts and bezoic hydrazide salts involves vapourization of the inhibitor in a nondissociated molecular form, followed by hydrolysis of salts into carboxylate anion ($RCOO^-$) and organic cations ($RCONHNH_3^+$). Anions are adsorbed onto anodic site of the metal and inhibit anodic reaction, whereas organic cations are adsorbed onto cathodic site, thereby preventing cathodic reaction (11).

Table 3.1.1 Name and structures of the compounds studied

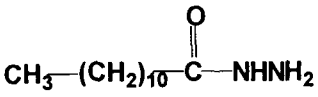
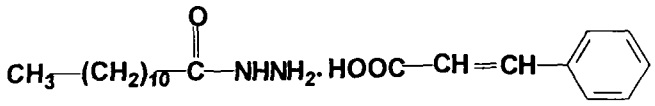
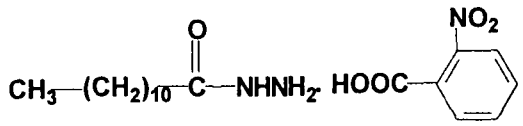
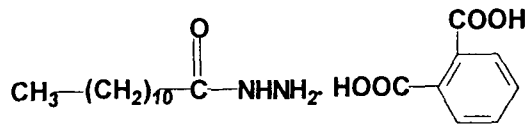
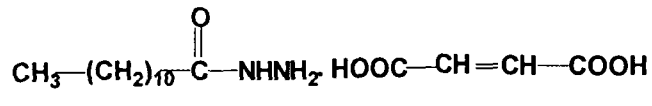
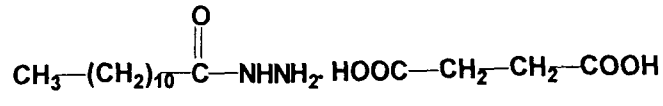
S.No.	Structure	Name and Abbreviation
1.		Lauric hydrazide (LH)
2.		Lauric hydrazide cinnamate (LHC)
3.		Lauric hydrazide nitrobenzoate (LHN)
4.		Lauric hydrazide phthalate (LHP)
5.		Lauric hydrazide maleate (LHM)
6.		Lauric hydrazide succinate (LHS)

Table 3.1.2 Name and structures of the compounds studied

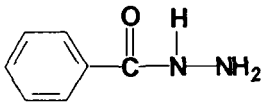
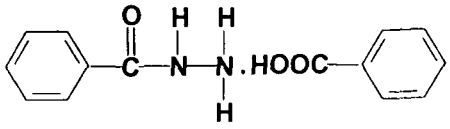
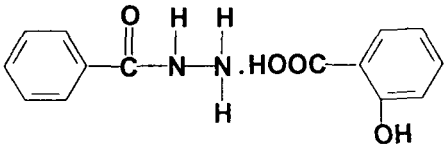
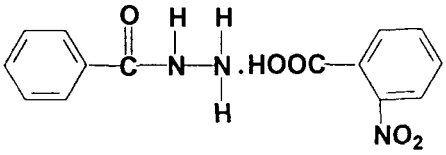
S.No.	Structure	Name and Abbreviation
1.		Benzoic hydrazide (BH)
2.		Benzoic hydrazide benzoate (BHB)
3.		Benzoic hydrazide salicylate (BHS)
4.		Benzoic hydrazide nitrobenzoate (BHN)

Table 3.1.3 Vapour pressure of VCIs at 40±1^{0}C for 30 days

S.No.	Compounds (VCIs)	Vapour pressure (mmHg)
1.	LH	1.40×10^{-6}
2.	LHC	6.01×10^{-7}
3.	LHNB	9.25×10^{-7}
4.	LHP	7.82×10^{-7}
5.	LHM	1.15×10^{-6}
6.	LHS	8.87×10^{-7}

Table 3.1.4 Vapour pressure of VCIs at 40±1^{0}C for 20 days

S.No.	Compounds (VCIs)	Vapour pressure (mmHg)
1.	BH	1.75×10^{-7}
2.	BHB	0.85×10^{-7}
3.	BHS	2.79×10^{-7}
4.	BHN	2.71×10^{-7}

Table 3.1.5 Weight loss parameters obtained for 1000 ppm concentration of lauric hyrazide and its salts at 40±1^{0}C and 90% relative humidity for 30 days for various metals

System	Weight loss (mg)	IE (%)	Corrosion Rate (mmpy × 10^{-2})
Mild steel			
Blank	38.5	-	5.95
LH	1.2	96.88	0.186
LHC	0.1	99.74	0.155
LHNB	0.4	98.96	0.620
LHP	0.6	98.44	1.29
LHM	0.8	97.14	1.24
LHS	1.1	97.14	1.70
Brass			
Blank	12.0	-	1.72
LH	1.4	88.33	0.201
LHC	0.3	97.50	0.043
LHNB	0.5	95.83	0.718
LHP	0.7	89.20	0.101
LHM	0.9	92.50	0.129
LHS	1.2	86.74	0.172
Copper			
Blank	9.7	-	1.317
LH	2.0	79.38	0.272
LHC	0.1	98.97	0.014
LHNB	0.2	97.94	0.027
LHP	0.8	91.75	0.109
LHM	1.2	87.63	0.163
LHS	1.6	83.51	0.217
Aluminum			
Blank	60.6	-	27.30
LH	3.5	94.22	1.58
LHC	0.8	98.68	0.360
LHNB	1.2	98.02	0.541
LHP	1.6	97.36	0.721
LHM	2.1	96.53	0.946
LHS	2.2	96.37	0.991
Zinc			
Blank	78.9	-	134.64
LH	3.2	95.94	0.546
LHC	1.5	98.10	0.256
LHNB	3.0	96.20	0.512
LHP	3.5	95.56	0.597
LHM	5.5	93.03	0.939
LHS	5.4	93.16	0.921

Table 3.1.6 Weight loss parameters obtained for 500 ppm concentration of benzoic hyrazide and its salts at 40±1^{0}C and 90% relative humidity for 20 days for various metals

System	Weight loss (mg)	IE (%)	Corrosion Rate (mmpy × 10^{-2})
Mild steel			
Blank	34.5	-	8.0
BH	1.2	96.6	0.27
BHB	1.2	96.6	0.27
BHS	1.3	96.2	0.30
BHN	2.4	93.1	0.55
Brass			
Blank	8.4	-	1.775
BH	0.3	96.4	0.062
BHB	0.3	96.4	0.062
BHS	0.5	94.0	0.105
BHN	0.9	89.2	0.190
Copper			
Blank	5.7	-	1.15
BH	0.2	96.5	0.04
BHB	0.2	96.5	0.04
BHS	0.5	91.2	0.10
BHN	1.0	82.4	0.20

Table 3.1.7 Results obtained from Eschke test for LHC at 40±1^{0}C and 90% relative humidity for 20 days for various metals

System	Visual observations	Corrosion Rate (mmpy × 10^{-2})
Mild steel (control)	Moderate to heavy rusting	0.550
LHC	No rusting, bright surface	0.033
Brass (control)	Moderate to heavy tarnishing	0.327
LHC	Slight tarnishing	0.030
Copper (control)	Moderate to heavy tarnishing	0.222
LHC	Slight tarnishing	0.020
Aluminum (control)	Heavy dulling, grayish white surface	6.22
LHC	Slight dulling	1.24

Table 3.1.8 Results obtained from Eschke test for BHB at 40±1^{0}C and 90% relative humidity for 20 days for various metals

System	Visual observations	Corrosion Rate (mmpy × 10^{-2})
Mild steel (control)	Moderate to heavy rusting	0.550
BHB	No rusting, bright surface	0.067
Brass (control)	Moderate to heavy tarnishing	0.327
BHB	Slight tarnishing	0.062
Copper (control)	Moderate to heavy tarnishing	0.222
BHB	Slight tarnishing	0.040

Table 3.1.9 Results obtained from salt inoculation test for LHC at 40±1^{0}C and 90% relative humidity for 20 days for various metals

System	Visual observations	Corrosion Rate (mmpy × 10^{-2})
Mild steel (control)	Whole surface covered with patches of brownish red spots	5.185
LHC	Rusting restricted to nuclei, rest of suface bright and unattacked	0.950
Brass (control)	Rusting around nuclei, heavy tarnishing	0.200
LHC	Slight rusting around nuclei	0.042
Copper (control)	Moderate to heavy tarnishing	0.427
LHC	Slight tarnishing	0.085
Aluminum (control)	Moderate corrosion around all nuclei, heavy dulling	5.90
LHC	Corrosion confined to nuclei, slight dulling	1.20

Table 3.1.10 Results obtained from salt inoculation test for BHB at 40±1^{0}C and 90% relative humidity for 20 days for various metals

System	Visual observations	Corrosion Rate (mmpy × 10^{-2})
Mild steel (control)	Whole surface covered with patches of brownish red	5.185
BHB	Rusting restricted to nuclei, rest of suface bright and unattacked	1.785
Brass (control)	Rusting around nuclei, heavy tarnishing	0.200
BHB	Slight rusting around nuclei	0.072
Copper (control)	Moderate to heavy tarnishing	0.427
BHB	Slight tarnishing	0.152

Table 3.1.11 Results obtained from SO_2 test for LHC at 40±1^{0}C and 90% relative humidity for 24 hours for various metals

System	Visual observations	Corrosion Rate (mmpy × 10^{-2})
Mild steel (control)	Severely rusted all over surface	12.52
LHC	No rusting, bright surface	0.150
Brass (control)	Moderate to heavy tarnishing	2.565
LHC	Slight tarnishing	0.340
Copper (control)	Heavy tarnishing	2.657
LHC	Slight tarnishing	0.380
Aluminum (control)	Slight dulling	5.40
LHC	No effect, bright surface	0.80

Table 3.1.12 Results obtained from SO_2 test for BHB at 40 ± 1^0C and 90% relative humidity for 24 hours for various metals

System	Visual observations	Corrosion Rate (mmpy × 10^{-2})
Mild steel (control)	Severely rusted all over surface	12.52
BHB	No rusting, bright surface	0.230
Brass (control)	Moderate to heavy tarnishing	2.565
BHB	Slight tarnishing	0.640
Copper (control)	Heavy tarnishing	2.657
BHB	Slight tarnishing	0.407

Table 3.1.13 Potentiodynamic polarization parameters obtained for 1000 ppm concentration of lauric hyrazide and its salts at 28±2^{0}C for various metals

System	E_{corr} (mV)	I_{corr} (mA cm^{-2})	IE (%)
Mild steel			
Blank	−562	0.25	-
LH	−430	0.032	87.20
LHC	−416	0.008	96.80
LHNB	−408	0.010	96.00
LHP	−450	0.018	92.80
LHM	−488	0.020	92.00
LHS	−480	0.026	89.60
Brass			
Blank	−340	0.20	-
LH	−270	0.026	87.00
LHC	−222	0.010	95.00
LHNB	−250	0.016	90.00
LHP	−260	0.014	93.00
LHM	−280	0.018	91.00
LHS	−236	0.024	88.00
Copper			
Blank	−190	0.16	-
LH	−150	0.024	85.00
LHC	−112	0.012	92.50
LHNB	−98	0.014	91.25
LHP	−124	0.024	85.00
LHM	−100	0.018	88.75
LHS	−165	0.020	87.50
Aluminum			
Blank	−680	0.30	-
LH	−654	0.038	87.33
LHC	−595	0.018	94.00
LHNB	−648	0.022	92.67
LHP	−640	0.020	96.60
LHM	−628	0.028	90.67
LHS	−610	0.030	90.00
Zinc			
Blank	−708	0.38	-
LH	−682	0.044	88.42
LHC	−616	0.020	94.74
LHNB	−638	0.024	93.68
LHP	−640	0.030	92.68
LHM	−670	0.028	92.63
LHS	−652	0.032	91.58

Table 3.1.14 Potentiodynamic polarization parameters obtained for 500 ppm concentration of benzoic hyrazide and its salts at 28±2^{0}C for various metals

System	E_{corr} (mV)	I_{corr} (mA cm^{-2})	IE (%)
Mild steel			
Blank	−562	0.25	-
BH	−432	0.042	83.20
BHC	−450	0.012	95.20
BHS	−480	0.022	91.20
BHN	−485	0.030	88.00
Brass			
Blank	−340	0.20	-
BH	−270	0.050	75.00
BHC	−285	0.018	91.00
BHS	−258	0.024	88.60
BHN	−282	0.030	85.00
Copper			
Blank	−190	0.16	-
BH	−160	0.048	70.00
BHC	−140	0.020	87.50
BHS	−148	0.024	85.00
BHN	−130	0.032	80.00

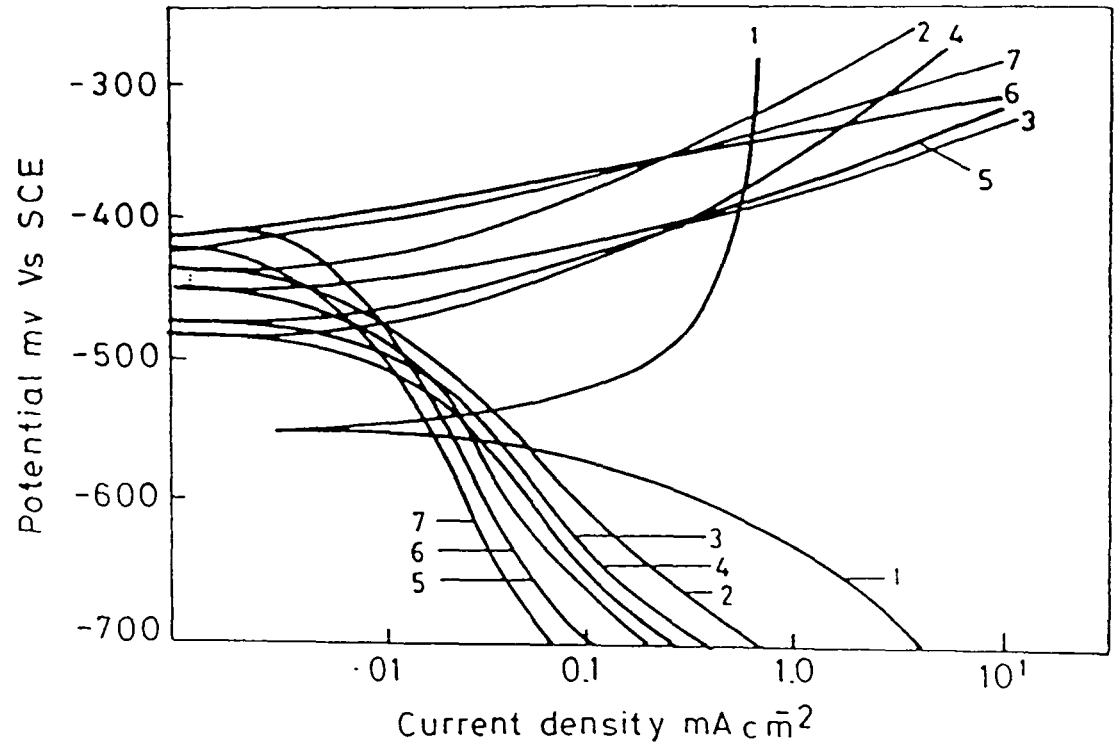


Figure 3.1.1A Potentiodynamic polarization curves for mild steel inhibited with vapour phase corrosion inhibitors 1. Blank, 2. LH, 3. LHNB, 4. LHP, 5. LHM, 6. LHS, 7. LHC

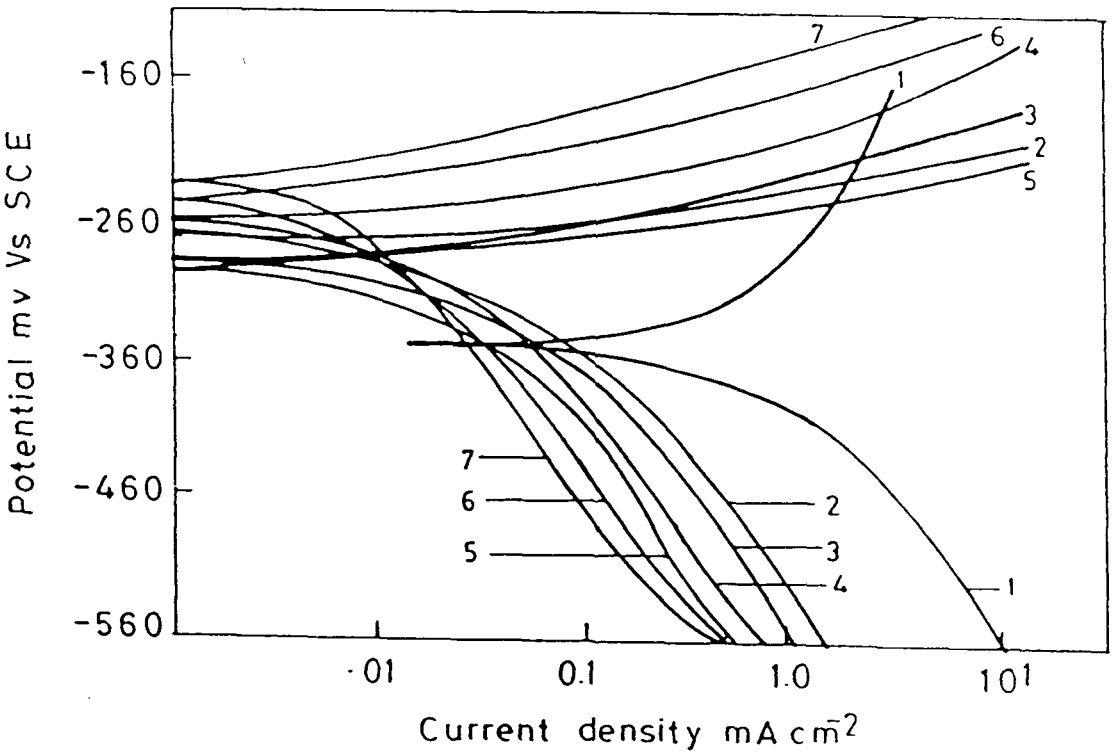


Figure 3.1.1B Potentiodynamic polarization curves for brass inhibited with vapour phase corrosion inhibitors 1. Blank, 2. LH, 3. LHNB, 4. LHP, 5. LHM, 6. LHS, 7. LHC

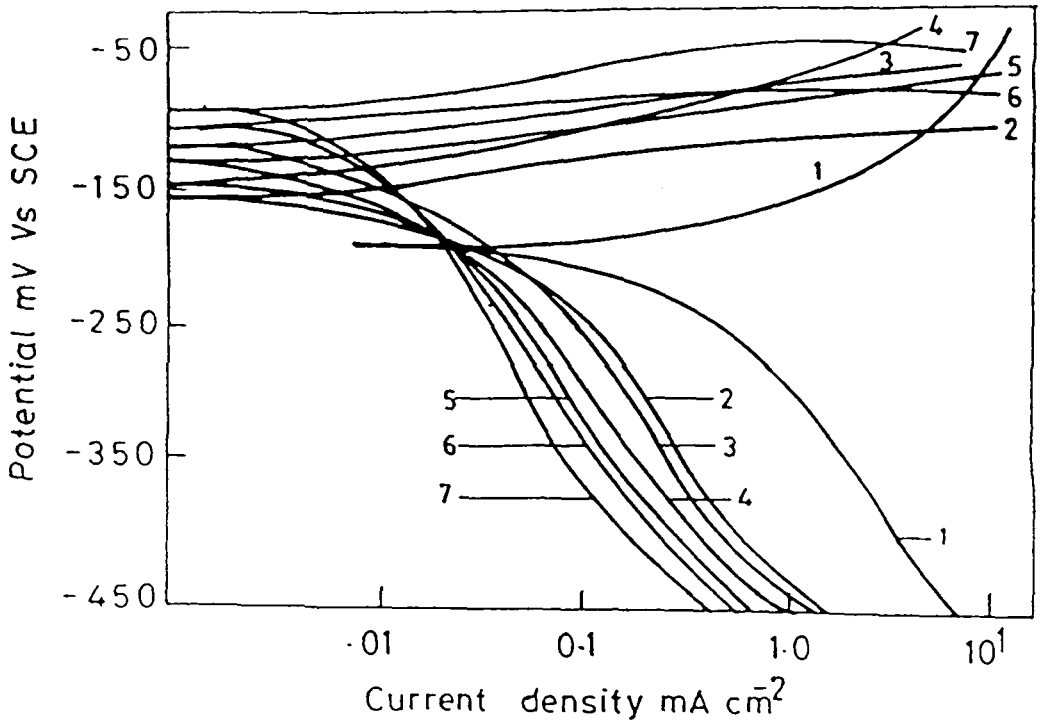


Figure 3.1.1C Potentiodynamic polarization curves for copper inhibited with vapour phase corrosion inhibitors 1. Blank, 2. LH, 3. LHNB, 4. LHP, 5. LHM, 6. LHS, 7. LHC

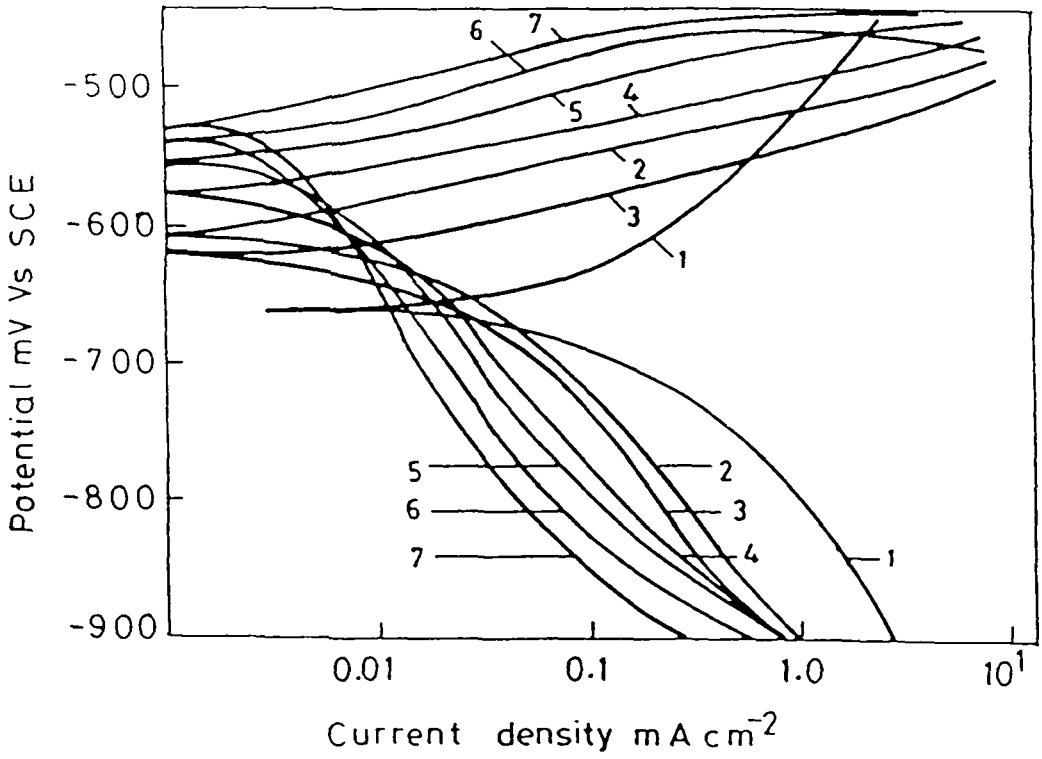


Figure 3.1.1D Potentiodynamic polarization curves for aluminum inhibited with vapour phase corrosion inhibitors 1. Blank, 2. LH, 3. LHNB, 4. LHP, 5. LHM, 6. LHS, 7. LHC

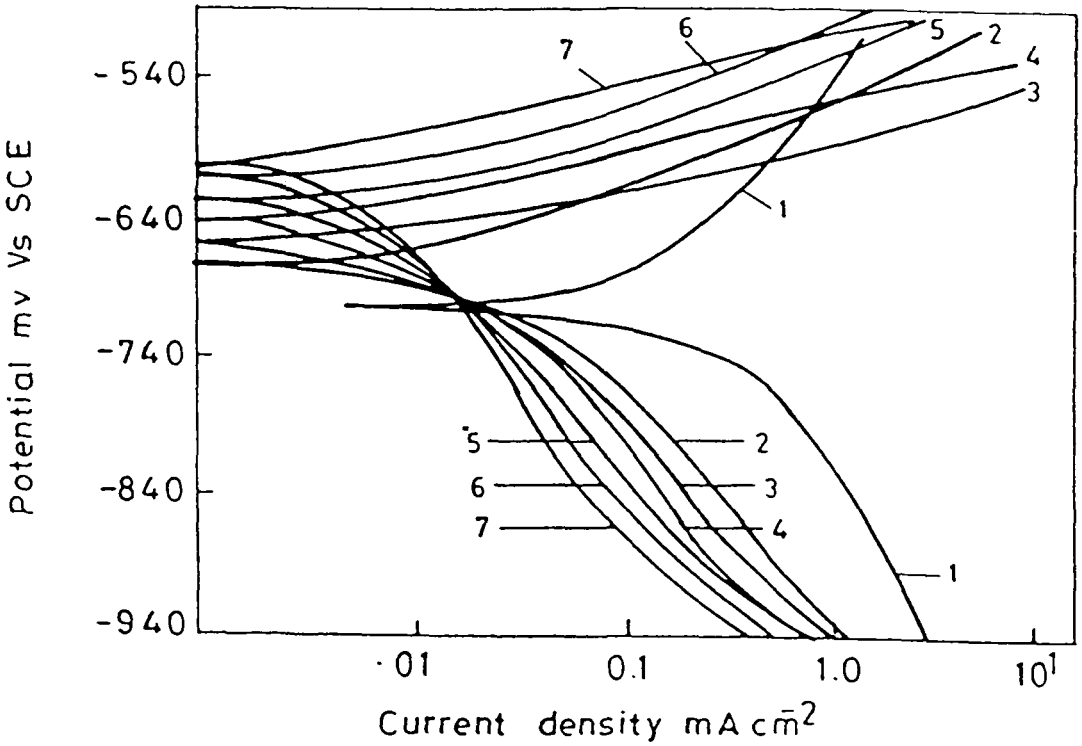


Figure 3.1.1E Potentiodynamic polarization curves for zinc inhibited with vapour phase corrosion inhibitors 1. Blank, 2. LH, 3. LHNB, 4. LHP, 5. LHM, 6. LHS, 7. LHC

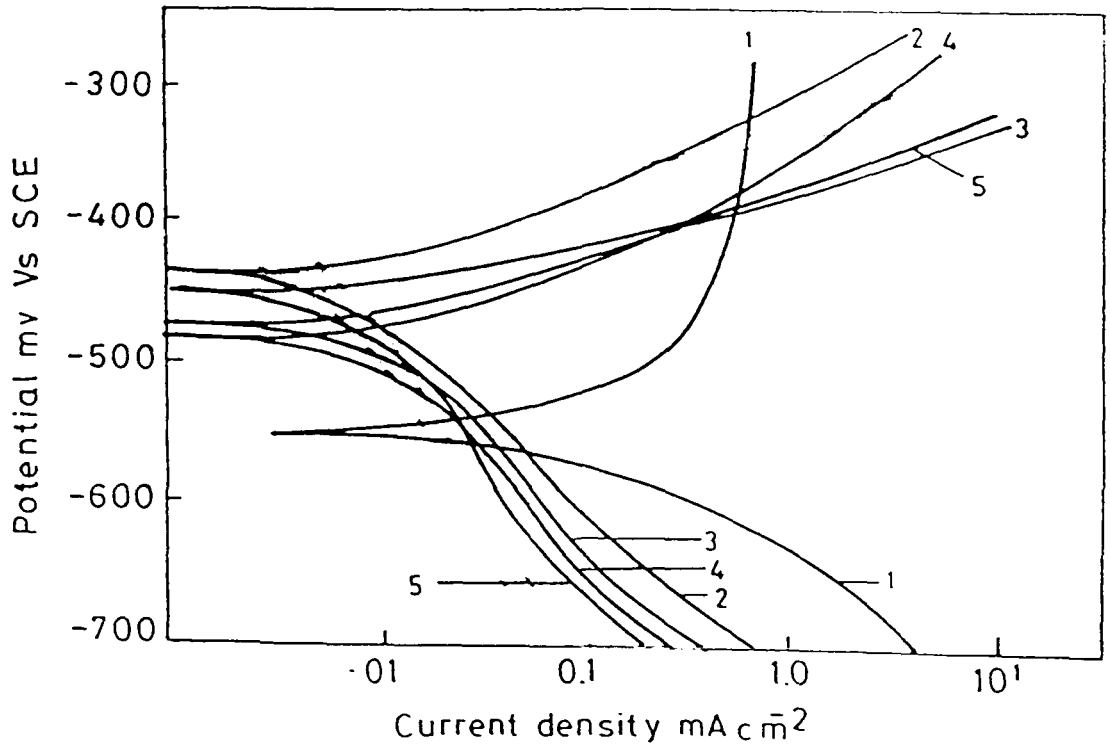


Figure 3.1.2A Potentiodynamic polarization curves for mild steel inhibited with vapour phase corrosion inhibitors 1. Blank, 2. BH, 3. BHN, 4. BHS, 5. BHB

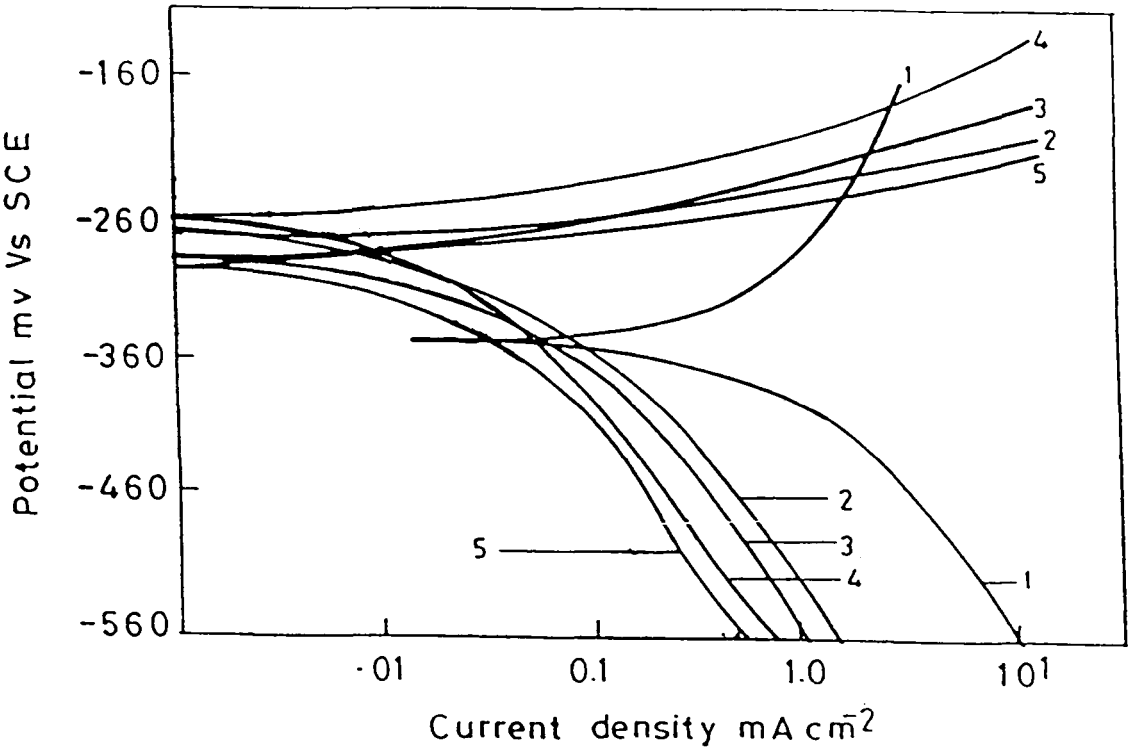


Figure 3.1.2B Potentiodynamic polarization curves for brass inhibited with vapour phase corrosion inhibitors 1. Blank, 2. BH, 3. BHN, 4. BHS, 5. BHB

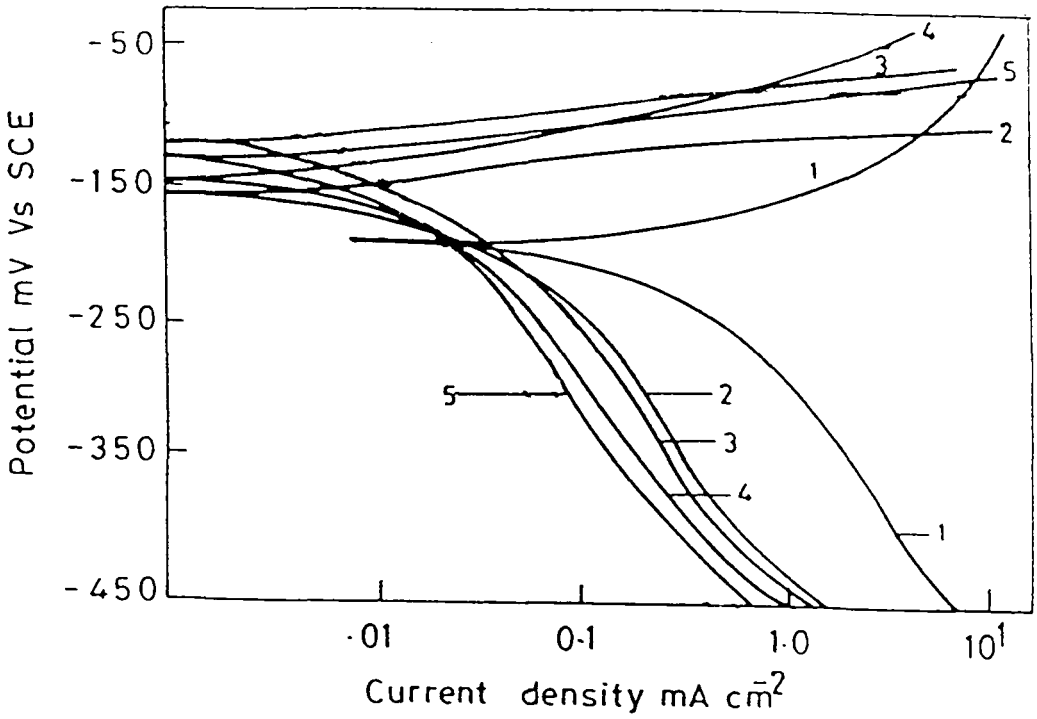


Figure 3.1.2C Potentiodynamic polarization curves for copper inhibited with vapour phase corrosion inhibitors 1. Blank, 2. BH, 3. BHN, 4. BHS, 5. BHB

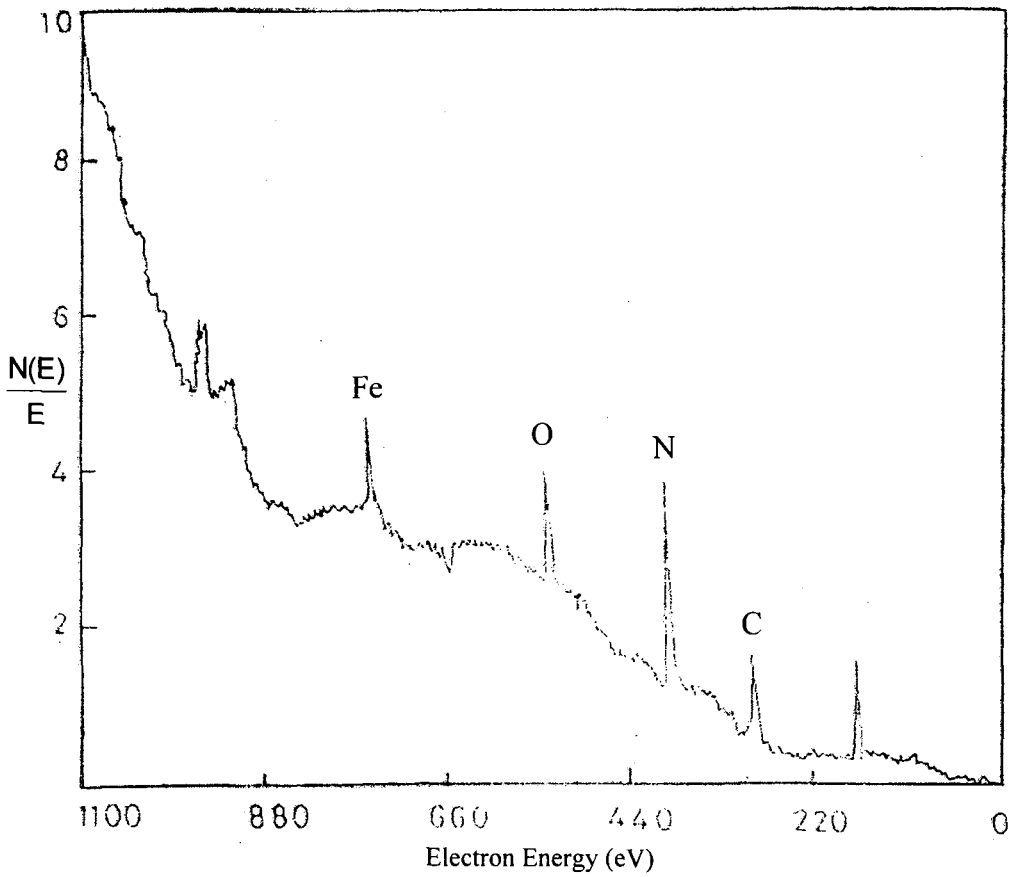


Figure 3.1.3 Auger electron spectra for mild steel inhibited with vapour phase corrosion inhibitor LHC

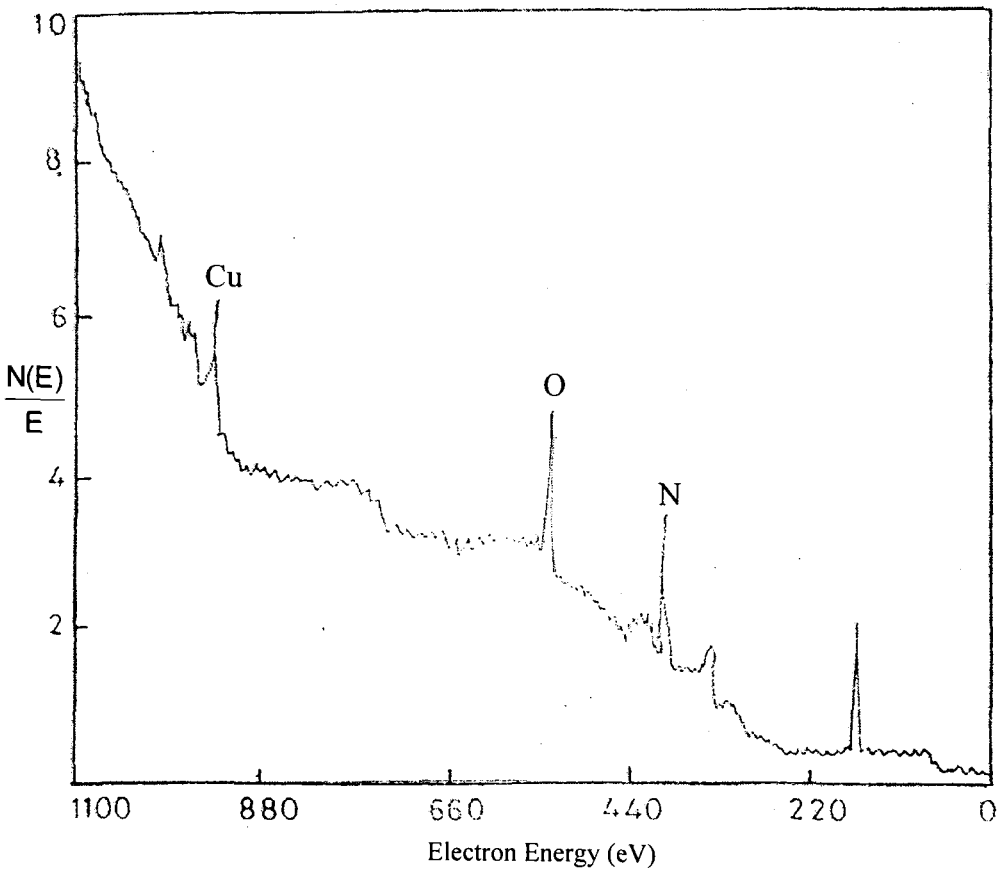


Figure 3.1.4 Auger electron spectra for copper inhibited with vapour phase corrosion inhibitor LHC

3A.1.10 Conclusion

i. All the vapour phase corrosion inhibitors (VCIs) showed good inhibition efficiency for mild steel, brass, copper, aluminum and zinc..

ii. Among all VCIs, LHC exhibited highest inhibition efficiency for all metals.

iii. All the inhibitors showed effective vapour pressure.

iv. All the vapour phase corrosion inhibitors inhibited corrosion of metals by being adsorbed onto the metal surface

v. All the investigated compounds behaved as anodic type inhibitors.

Section – 2

Schiff's Bases
as
Vapour-Phase Corrosion Inhibitors (VCIs)

Schiff's bases have been reported as effective vapour phase corrosion inhibitors for the protection of metals (13,14).

In the present study the influence of some schiff's bases as vapour phase corrosion inhibitors (VCIs) on corrosion of mild steel, brass, copper, under vapour phase conditions has been investgated by weight loss method, Eschke test, salt inoculation test, sulfur dioxide test and potentiodynamic polarization method. The vapour pressure of the compounds was determined by Knudsen method.

3A.2.1 Corrosion Inhibitors

The molecular structure and other details of the compounds used as vapour phase corrosion inhibitors (VCIs) are given in Table 3.2.1 and Table 3.2.2 respectively.

3A.2.2 Vapour Pressure Determination

The values of vapour pressure of schiff's bases of lauric hydrazide and shiff's bases of benzoic hydrazide, at 40 ± 1^{0}C for 20 days obtained from Knudsen method are summarized in Table 3.2.3 and Table 3.2.4 respectively .

3A.2.3 Weight Loss Studies

The various parameters such as percentage inhibition efficieny (%I.E) and corrosion rate (C.R) of different metals uder vapour phase condition in absence and presence of schiff's bases of lauric hydrazide and shiff's bases of benzoic hydrazide, at 500 ppm concentration, at $40\pm1\ ^{0}$ C and 90% relative humidity are summarized in Table 3.2.5 and Table 3.2.6 respectively. It has been observed from the results that all the compounds inhibit corrosion of mild steel, brass, copper. The inhibition efficiency for all these compounds is found good at 500 ppm of schiff's bases of lauric hydrazide and shiff's bases of benzoic hydrazide and to give maximum efficiency.

The order of inhibition efficiency of examined VCIs has been found as follows :

CLH > SLH

BBH > SHH > CBH

The effectiveness of a given compounds as corrosion inhibitors depends on the structure of the organic compounds (9). The variation of inhibition efficiency mainly depends on the type and nature of the substituents present in the inhibitor (10).The corrosion inhibiting action of the VCIs is attributed to the presence of lone pair of electrons present on N atoms of the inhibitors, which facilitate adsorption for these inhibitors onto the metal surface. Thus on the basis of the above mentioned factors, the difference in protective action of VCIs can be explained.

The inhibition of corrosion by Schiff's bases may be explain on the basis of the presence of π electrons of benzene ring and azomethine group (-C=N-), which facilitates adsorption of molecules onto metal surface. CLH exhibited the better performance than SLH due to presence of additional π bond between carbon atoms (-C=C-), conjugated to azomethine group (-C=N-).

BBH showed good inhibition efficiency due to the presence of extensively delocalized π electrons in benzene ring further facilitates the adsorption process. The lower inhibition efficiency of SBH, CBH, may be attributed to the orientation of the substituent group,which prevents a flat orientation on the metal surface causing less adsorption.

3A.2.4 Eschke Test

The results obtained by this test in absence (control) and presence of CLH and BBH at 40 ± 1^0C and 90% relative humidity for 20 days for various metals are given in Table 3.2.7 and Table 3.2.8 respectively. The results show that minimum corrosion is taking place in presence of both CLH and BBH.

3A.2.5 Salt Inoculation Test

The results obtained when the metals are inoculated with sodium chloride in absence (control) and presence of CLH and BBH at 40 ± 1^0C and 90% relative humidity for 20 days for various metals are shown in Table 3.2.9 and Table 3.2.10 respectively.The results show that number of nucleation is minimize in inhibiting metal coupons containing CLH and BBH.

3A.2.6 Sulfur dioxide (SO_2) Test

The results obtained by this test in absence(control) and presence of CLH and BBH at 40±1^{0}C and 90% relative humidity for 24 hours for various metals are shown in Table 3.2.11 and Table 3.2.12 respectively. It has been observed from the results that both the compounds CLH and BBH inhibit corrosion of various metals.

3A.2.7 Potentiodynamic Polarization Studies

The corrosion parameters such as corrosion current density(I_{corr}), corrosion potential(E_{corr}) and percentage of inhibition efficiency (%IE) obtained from the potentiodynamic polarization curves in absence and presence of shiff's bases of lauic hydrazide and shiff's bases of benzoic hydrazide and at 500 ppm concentration, at 28±2 ^{0} C are given in Table 3.2.13 and Table 3.2.14 .

Potentiodynamic polarization studies were carried out by immersing metal coupons and inhibited coupons in a 1 N Na_2SO_4 solution (11). The I_{corr} value was found to decrease significantly in presence of inhibitors, indicating that the compounds were effective corrosion inhibitors. All of these compounds shifted the E_{corr} in a more positive direction, suggesting that they were predominantly anodic inhibitors. Figures 3.2.1 A –C and figure 3.2.2 A-C show the Tafel plots obtained from different inhibited coupons in presence of the 1 N Na_2SO_4 solution for mild steel, brass, copper.

Guo Gao et al. (12) studied some organic compounds tested as VCIs for brass in simulated atmospheric water using potentiodynamic polarization method. Polarization curves showed that the compounds acted as good anodic inhibitor.

Table 3.2.1 Name and structures of the compounds studied

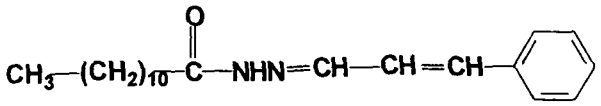
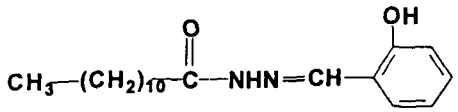
S.No.	Structure	Name and Abbreviation
1.		Cinnamylidene lauric hydrazide (CLH)
2.		Salicylidene lauric hydrazide (SLH)

Table 3.2.2 Name and structures of the compounds studied

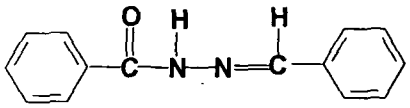
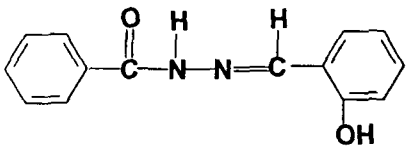
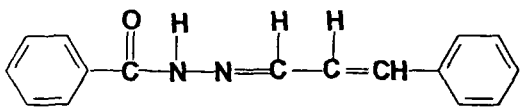
S.No.	Structure	Name and Abbreviation
1.		Benzalidene bezoic hydrazide (BBH)
2.		Salicylidene benzoic hydrazide (SBH)
3.		Cinamalidene benzoic hydrazide (CBH)

Table 3.2.3 Vapour pressure of VCIs at 40±1^{0}C for 20 days

S.No.	Compounds (VCIs)	Vapour pressure (mmHg)
1.	CLH	0.86×10^{-8}
2.	SLH	1.73×10^{-8}

Table 3.2.4 Vapour pressure of VCIs at 40±1^{0}C for 20 days

S.No.	Compounds (VCIs)	Vapour pressure (mmHg)
1.	BBH	5.98×10^{-7}
2.	SBH	8.68×10^{-7}
3.	CBH	0.85×10^{-7}

Table 3.2.5 Weight loss parameters obtained for 500 ppm concentration of schiff's bases of lauric hydrazide at 40±1^{0}C and 90% relative humidity for 20 days for various metals

System	Weight loss (mg)	IE (%)	Corrosion Rate (mmpy × 10^{-2})
Mild steel			
Blank	34.5	-	8.00
CLH	1.2	96.62	0.28
SLH	1.5	95.75	0.35
Brass			
Blank	8.4	-	1.775
CLH	0.5	94.04	0.105
SLH	0.8	90.71	0.17
Copper			
Blank	5.7	-	1.15
CLH	0.4	93.02	0.081
SLH	0.6	89.65	0.120

Table 3.2.6 Weight loss parameters obtained for 500 ppm concentration of shiff's bases of benzoic hyrazide at 40±1^{0}C and 90% relative humidity for 20 days for various metals

System	Weight loss (mg)	IE (%)	Corrosion Rate (mmpy × 10^{-2})
Mild steel			
Blank	34.5	-	8.0
BBH	1.0	97.12	0.23
SBH	1.2	96.62	0.27
CBH	1.8	94.87	0.41
Brass			
Blank	8.4	-	1.775
BBH	0.3	96.46	0.062
SBH	0.5	94.04	0.105
CBH	0.9	89.26	0.190
Copper			
Blank	5.7	-	1.15
BBH	0.3	94.75	0.060
SBH	0.4	93.02	0.081
CBH	0.5	91.22	0.102

Table 3.2.7 Results obtained from Eschke test for CLH at 40±1^{0}C and 90% relative humidity for 20 days for various metals

System	Visual observations	Corrosion Rate (mmpy × 10^{-2})
Mild steel (control)	Moderate to heavy rusting	0.550
CLH	No rusting, bright surface	0.033
Brass (control)	Moderate to heavy tarnishing	0.327
CLH	Slight tarnishing	0.030
Copper (control)	Moderate to heavy tarnishing	0.222
CLH	Slight tarnishing	0.020

Table 3.2.8 Results obtained from Eschke test for BBH at 40±1^{0}C and 90% relative humidity for 20 days for various metals

System	Visual observations	Corrosion Rate (mmpy × 10^{-2})
Mild steel (control)	Moderate to heavy rusting	0.550
BBH	2-4rusted spots, rest bright surface	0.069
Brass (control)	Moderate to heavy tarnishing	0.327
BBH	Slight tarnishing	0.084
Copper (control)	Moderate to heavy tarnishing	0.222
BBH	Slight to moderate tarnishing	0.081

Table 3.2.9 Results obtained from salt inoculation test for CLH at 40±1^{0}C and 90% relative humidity for 20 days for various metals

System	Visual observations	Corrosion Rate (mmpy × 10^{-2})
Mild steel (control)	Whole surface covered with patches of brownish red	5.185
CLH	Rusting restricted to nuclei, rest of suface bright and unattacked	0.950
Brass (control)	Rusting around nuclei, heavy tarnishing	0.200
CLH	Slight rusting around nuclei	0.042
Copper (control)	Moderate to heavy tarnishing	0.427
CLH	Slight tarnishing	0.085

Table 3.2.10 Results obtained from salt inoculation test for BBH at 40±1^{0}C and 90% relative humidity for 20 days for various metals

System	Visual observations	Corrosion Rate (mmpy × 10^{-2})
Mild steel (control)	Whole surface covered with patches of brownish red	5.185
BBH	Rusting restricted to nuclei, rest of suface almost bright and unattacked	2.401
Brass (control)	Rusting around nuclei, heavy tarnishing	0.200
BBH	Slight rusting around nuclei	0.074
Copper (control)	Rusting around nuclei, heavy tarnishing	0.427
BBH	Slight rusting around nuclei, slight tarnishing	0.204

Table 3.2.11 Results obtained from SO_2 test for CLH at 40±1^{0}C and 90% relative humidity for 24 hours for various metals

System	Visual observations	Corrosion Rate (mmpy × 10^{-2})
Mild steel (control)	Severely rusted all over surface	12.52
CLH	No rusting, bright surface	0.150
Brass (control)	Moderate to heavy tarnishing	2.565
CLH	Slight tarnishing	0.340
Copper (control)	Heavy tarnishing	2.657
CLH	Slight tarnishing	0.380

Table 3.2.12 Results obtained from SO_2 test for 500 BBH at 40±1^{0}C and 90% relative humidity for 24 hours for various metals

System	Visual observations	Corrosion Rate (mmpy × 10^{-2})
Mild steel (control)	Severely rusted all over surface	12.52
BBH	Small rusted spots allover surface	1.60
Brass (control)	Moderate to heavy tarnishing	2.565
BBH	Slight tarnishing	0.213
Copper (control)	Heavy tarnishing	2.657
BBH	Slight tarnishing	0.204

Table **3.2.13** Potentiodynamic polarization parameters obtained for 500 ppm concentration of shiff's bases of lauric hyrazide at 28±2^{0}C for various metals

System	E_{corr} (mV)	I_{corr} (mA cm^{-2})	IE (%)
Mild steel			
Blank	−562	0.25	-
CLH	−480	0.012	95.20
SLH	−490	0.014	94.40
Brass			
Blank	−340	0.20	-
CLH	−290	0.018	91.00
SLH	−280	0.022	89.00
Copper			
Blank	−190	0.16	-
CLH	−145	0.014	91.25
SLH	−150	0.020	87.50

Table 3.2.14 Potentiodynamic polarization parameters obtained for 500 ppm concentration of shiff's bases of benzoic hyrazide at 28±2^{0}C for various metals

System	E_{corr} (mV)	I_{corr} (mA cm^{-2})	IE (%)
Mild steel			
Blank	−562	0.25	-
BBH	−425	0.010	96.00
SBH	−440	0.016	93.60
CBH	−405	0.018	92.80
Brass			
Blank	−340	0.20	-
BBH	−270	0.010	95.00
SBH	−285	0.016	90.00
CBH	−260	0.026	87.00
Copper			
Blank	−190	0.16	-
BBH	−145	0.012	92.00
SBH	−125	0.014	91.25
CBH	−158	0.024	85.00

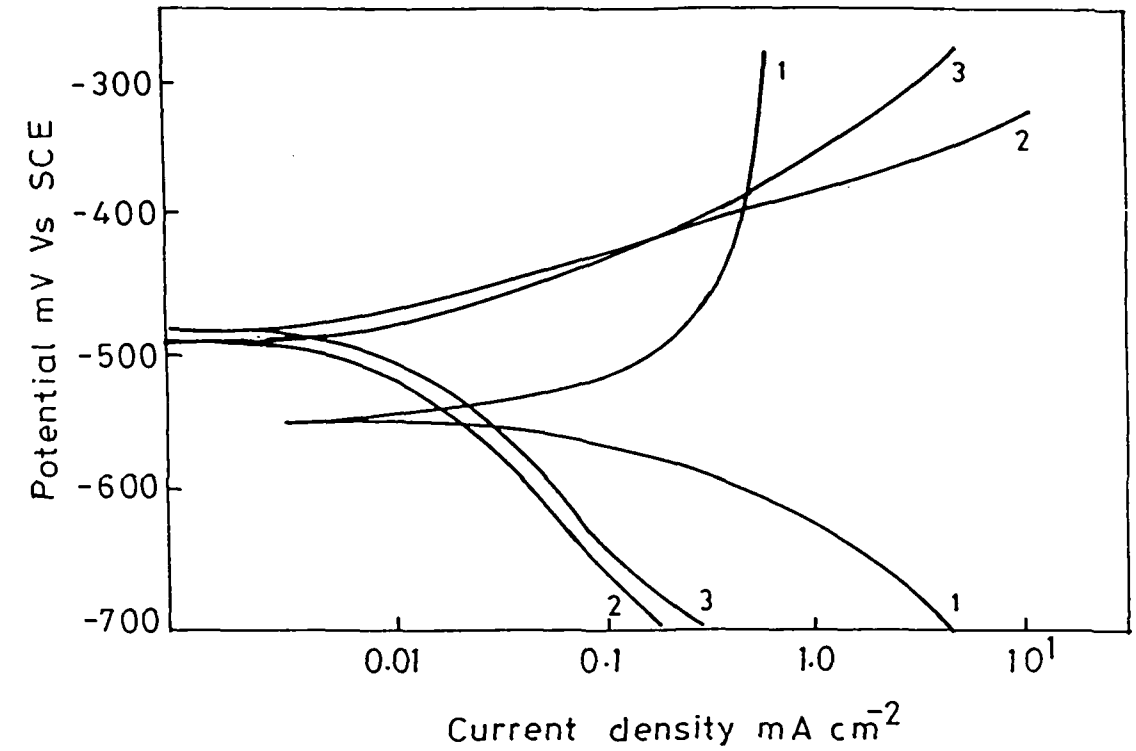


Figure 3.2.1A Potentiodynamic polarization curves for mild steel inhibited with vapour phase corrosion inhibitors 1. Blank, 2. SLH, 3. CLH

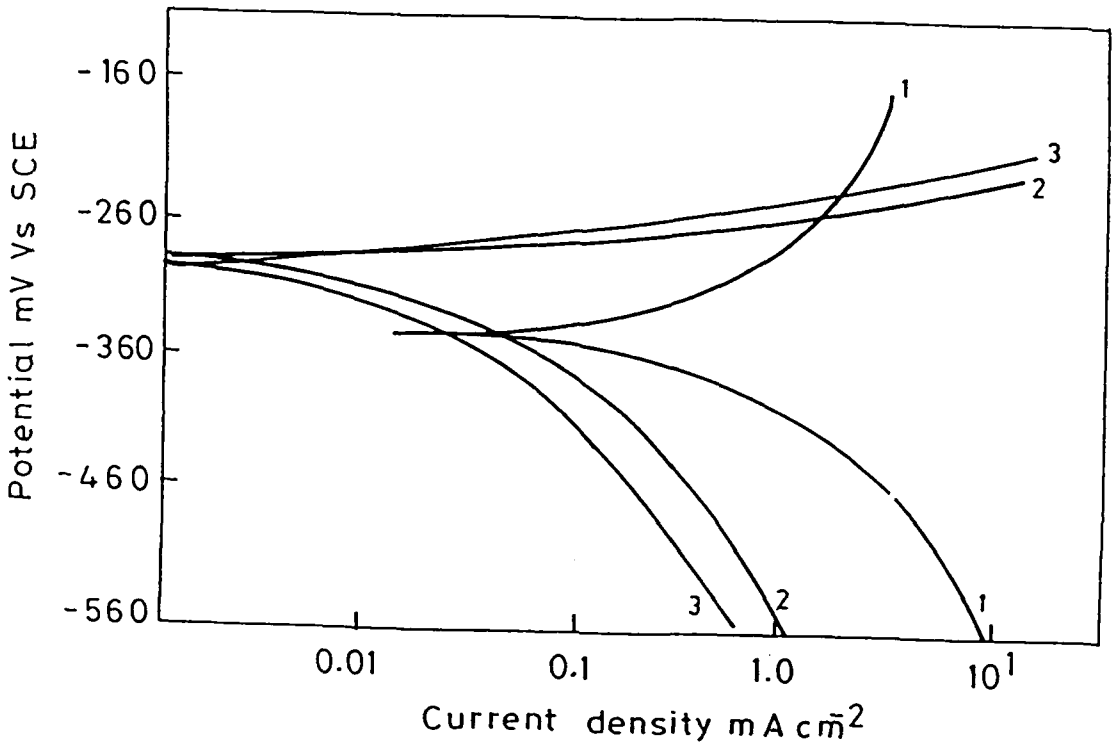


Figure 3.2.1B Potentiodynamic polarization curves for brass inhibited with vapour phase corrosion inhibitors 1. Blank, 2. SLH, 3. CLH

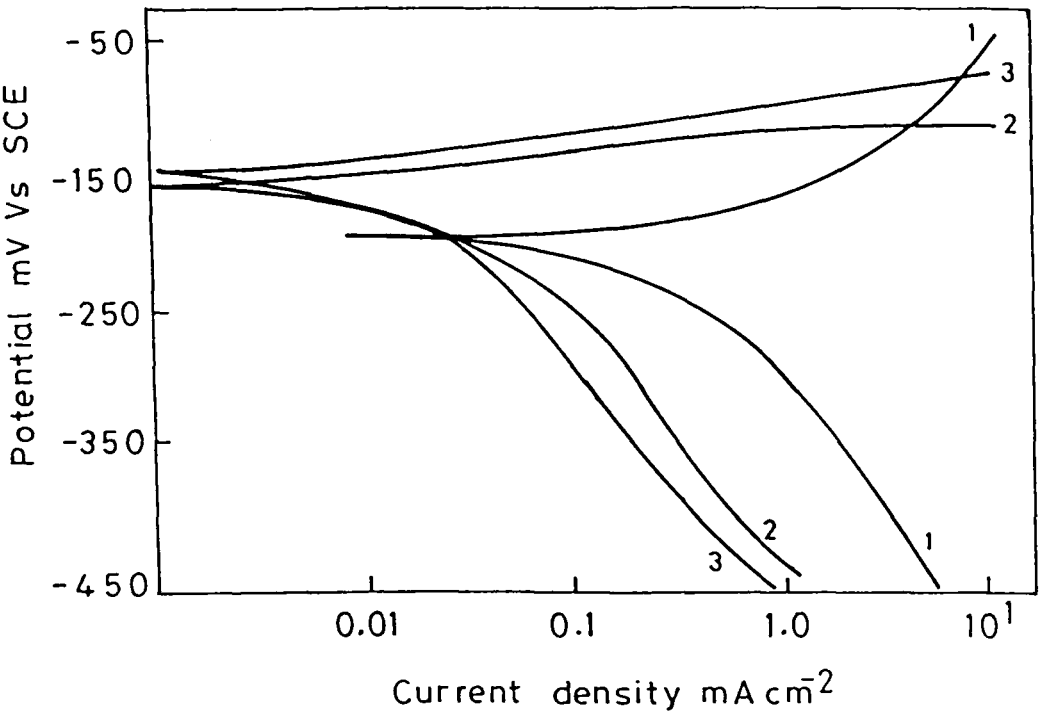


Figure 3.2.1C Potentiodynamic polarization curves for copper inhibited with vapour phase corrosion inhibitors 1. Blank, 2. SLH, 3. CLH

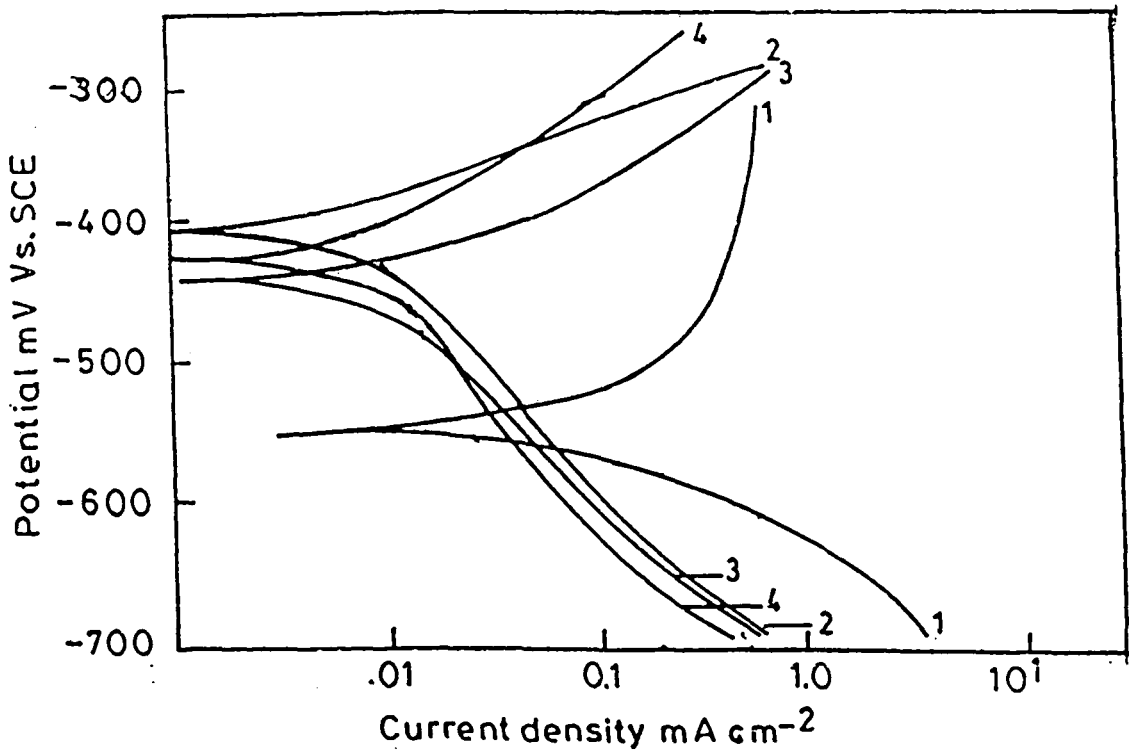


Figure 3.2.2A Potentiodynamic polarization curves for mild steel inhibited with vapour phase corrosion inhibitors 1. Blank, 2. CBH, 3. SBH, 4. BBH

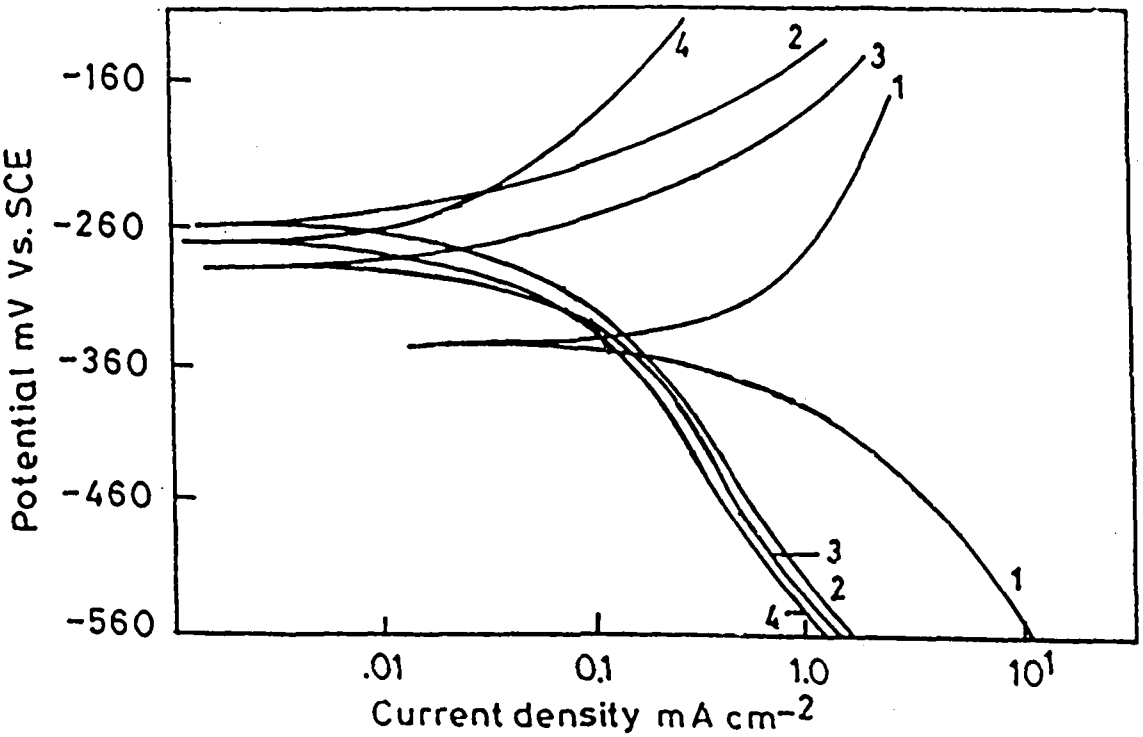


Figure 3.2.2B Potentiodynamic polarization curves for brass inhibited with vapour phase corrosion inhibitors 1. Blank, 2. CBH, 3. SBH, 4. BBH

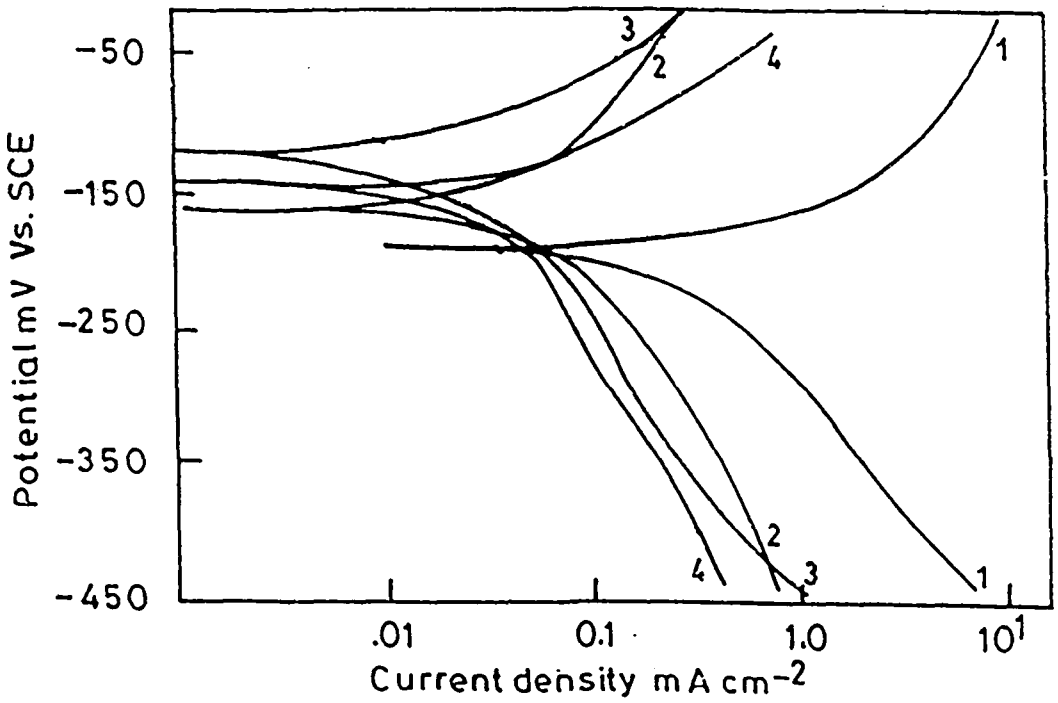


Figure 3.2.2C Potentiodynamic polarization curves for copper inhibited with vapour phase corrosion inhibitors 1. Blank, 2. CBH, 3. SBH, 4. BBH

3A.2.8 Conclusion

i. All the tested vapour phase corrosion inhibitors showed good inhibition efficiency for mild steel, brass and copper.

ii. All the organic compound exhibited effective vapour pressure.

iii. All the vapour phase corrosion inhibitors inhibited corrosion of metals by being adsorbed onto the metal surface.

iv. All the compounds behaved as anodic type inhibitors.

Section – 3

Imidazoline Salts
as
Vapour-Phase Corrosion Inhibitors (VCIs)

Numerous investigations have been reported corrosion inhibition by imidazoline derivatives as vapour phase corrosion inhibitors for various industrial metals and alloys (15-18).

In the present study the influence of some imidazoline salts as vapour phase corrosion inhibitors (VCIs) on corrosion of mild steel, brass, copper, aluminum under vapour phase conditions has been investgated by weight loss method , Eschke test, salt inoculation test, sulfur dioxide test and potentiodynamic polarization method. The vapour pressure of the compounds was determined by Knudsen method.

3A.3.1 Corrosion Inhibitors

The molecular structure and other details of the compounds used as vapour phase corrosion inhibitors (VCIs) are given in Table 3.3.1 and Table 3.3.2 respectively.

3A.3.2 Vapour Pressure Determination

The values of vapour pressure of 1-(2-aminoethyl)-2 dec-9 enyl-2-imidazoline salts and 1-(2-aminooethyl)-2 undecyl-2-imidazoline salts, at 40 ± 1^{0}C for 20 days obtained from Knudsen method are summarized in Table 3.3.3 and Table 3.3.4 respectively .

3A.3.3 Weight Loss Studies

The various parameters such as percentage inhibition efficieny (%I.E) and corrosion rate (C.R) of different metals uder vapour phase condition in absence and presence of 1-(2-aminoethyl)-2 dec-9 enyl-2-imidazoline salts and 1-(2-aminoethyl)-2 undecyl-2-imidazole salts at 500 ppm concentration, at $40\pm1\ ^{0}$ C and 90% relative humidity are summarized in Table 3.3.5 and Table 3.3.6 respectively. It has been observed from the results that all the compounds inhibit corrosion of mild steel, brass, copper and aluminum. The inhibition efficiency for all these compounds is found good a at 500 ppm concentration to give maximum efficiency.

The order of inhibition efficiency of examined VCIs has been found as follows :

ADIC > ADIP > ADIN > ADIS

AUIC > AUIP > AUIN > AUIM

The effectiveness of a given compounds as corrosion inhibitors depends on the structure of the organic compounds (9). The variation of inhibition efficiency mainly depends on the type and nature of the substituents present in the inhibitor (10).The corrosion inhibiting action of VCIs is attributed to the presence of lone pair of electrons present on N atoms of the inhibitor molecules, which facilitate adsorption for these inhibitors onto the metal surface. Thus on the basis of the above mentioned factors, the difference in protective action of VCIs can be explained.

The corrosion inhibiting action of the imidazoline salts is attributed to the presence of lone pair of electrons present on the N atoms of the inhibitor molecules, which facilitate adsorption onto metal surface. Cinnamate salts of imidazoline exhibited highest inhibition efficiency for ferrous and non-ferrous metals may be attributed to the presence of an additional π bond between carbon atoms(-C=C-) which further facilitate greater adsorption onto metal surface.The inhibitive action of phthalate of imidazoline is attributed to the presence of of an additional aromatic ring. The corrosion inhibiting effect of the nitrobenzoate is attributed to the presence of a nitro group The inhibiting effect of maleate of imidazoline is attributed to the presence of a double bond between the caron atoms (-C=C-) through which they adsorb strongly onto the surface of metals. The inhibiting action of salicylate of imidazoline is attributed to the presence of OH group.

3A.3.4 Eschke Test

The results obtained by this test in absence(control) and presence of ADIC and AUIC at 40±1^{0}C and 90% relative humidity for 20 days for various metals are given in Table 3.3.7 and Table 3.3.8 respectively. The results show that minimum corrosion is taking place in presence of both ADIC and AUIC.

3A.3.5 Salt Inoculation Test

The results obtained when the metals are inoculated with sodium chloride in absence (control) and presence of ADIC and AUIC at 40±1^{0}C and 90% relative humidity for

20 days for various metals are shown in Table 3.3.9 and Table 3.3.10 respectively.The results show that number of nucleation is minimize in inhibiting metal coupons containing ADIC and AUIC.

3A.3.6 Sulfur dioxide (SO_2) Test

The results obtained by this test in absence(control) and presence of ADIC and AUIC at 40±1^{0}C and 90% relative humidity for 24 hours for various metals are shown in Table 3.3.11 and Table 3.3.12 respectively. It has been observed from the results that both the compounds ADIC and AUIC inhibit corrosion of various metals.

3A.3.7 Potentiodynamic Polarization Studies

The corrosion parameters such as corrosion current density(I_{corr}), corrosion potential(E_{corr}) and percentage of inhibition efficiency (%IE) obtained from the potentiodynamic polarization curves in absence and presence of 1-(2-aminoethyl)-2 dec-9 enyl-2-imidazoline salts and 1-(2-aminoethyl)-2 undecyl-2-imidazole salts,at 500 ppm concentration, at 28±2 ^{0} C are given in Table 3.3.13 and Table 3.3.14 .

Potentiodynamic polarization studies were carried out by immersing metal coupons and inhibited coupons in a 1 N Na_2SO_4 solution (11). The I_{corr} value was found to decrease significantly in presence of inhibitors, indicating that the compounds were effective corrosion inhibitors. All of these compounds shifted the E_{corr} in a more positive direction, suggesting that they were predominantly anodic inhibitors. Figures 3.3.1 A-D and figure 3.3.2 A-D show the Tafel plots obtained from different inhibited coupons in presence of the 1 N Na_2SO_4 solution for mild steel, brass, copper, aluminum and zinc.

Guo Gao et al. studied some organic compounds tested as VCIs for brass in simulated atmospheric water using potentiodynamic polarization method. Polarization curves showed that the compounds acted as good anodic inhibitor.

3A.3.8 Mechanism of Corrosion Inhibition

Inhibition of metallic corrosion in presence of 1-(2-aminoethyl)-2 dec-9 enyl-2-imidazoline salts and 1-(2-aminoethyl)-2 undecyl-2-imidazoline salts involves vapourization of the inhibitor in a nondissociated molecular form, followed by hydrolysis of salts into carboxylate anion ($RCOO^-$) and organic cations ($RCONHNH_3^+$). Anions are adsorbed onto anodic site of the metal and inhibit anodic reaction, whereas organic cations are adsorbed onto cathodic site, thereby preventing cathodic reaction (11).

Table 3.3.1 Name and structures of the compounds studied

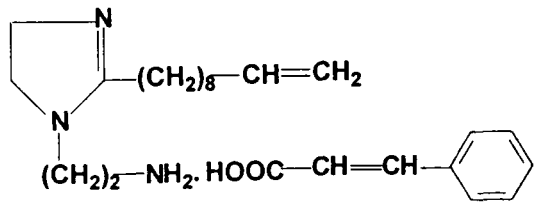
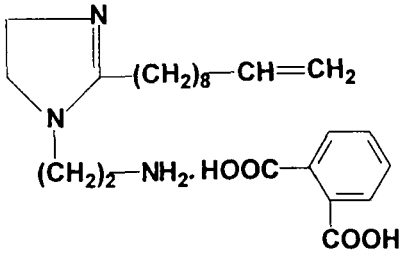
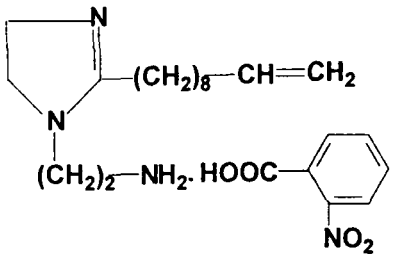
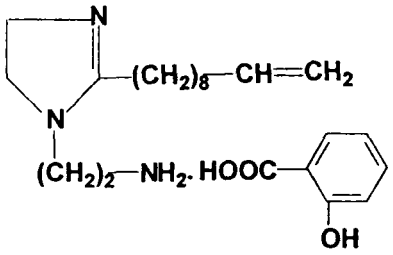
S.No.	Structure	Name and Abbreviation
1.		1-(2-aminoethyl)-2 dec-9 enyl-2 imidazoline cinnamate (ADIC)
2.		1-(2-aminoethyl)-2 dec-9 enyl-2 imidazoline phthalate (ADIP)
3.		1-(2-aminoethyl)-2 dec-9 enyl-2 imidazoline nitrobenzoate (ADIN)
4.		1-(2-aminoethyl)-2 dec-9 enyl-2 imidazoline salicylate (ADIS)

Table 3.3.2 Name and structures of the compounds studied

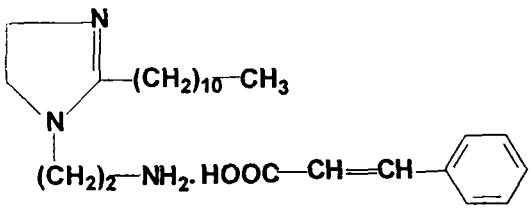
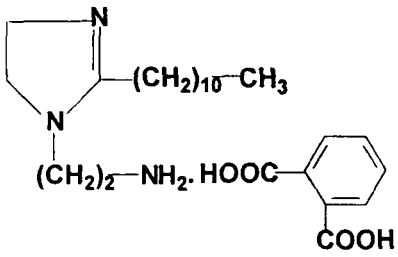
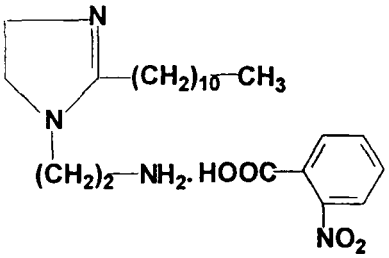
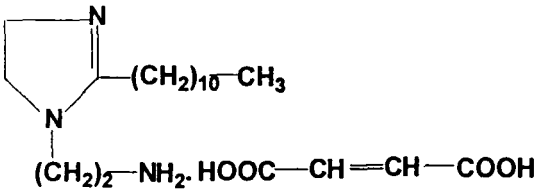
S.No.	Structure	Name and Abbreviation
1.		1-(2-aminoethyl)-2 undecyl-2 imidazoline cinnamate (AUIC)
2.		1-(2-aminoethyl)-2 undecyl-2 imidazoline phthalate (AUIP)
3.		1-(2-aminoethyl)-2 undecyl-2 imidazoline nitrobenzoate (AUIN)
4.		1-(2-aminoethyl)-2 undecyl-2 imidazoline maleate (AUIM)

Table 3.3.3 Vapour pressure of VCIs at 40±1^{0}C for 20 days

S.No.	Compounds (VCIs)	Vapour pressure (mmHg)
1.	ADIC	1.36×10^{-5}
2.	ADIP	1.58×10^{-6}
3.	ADIN	6.90×10^{-6}
4.	ADIS	9.10×10^{-6}

Table 3.3.4 Vapour pressure of VCIs at 40±1^{0}C for 20 days

S.No.	Compounds (VCIs)	Vapour pressure (mmHg)
1.	AUIC	6.90×10^{-6}
2.	AUIP	7.40×10^{-6}
3.	AUIN	5.60×10^{-6}
4.	AUIM	1.45×10^{-5}

Table 3.3.5 Weight loss parameters obtained for 500 ppm concentration of 1-(2-aminoethyl)-2 dec-9 enyl-2-imidazoline salts at 40±1^{0}C and 90% relative humidity for 20 days for various metals

System	Weight loss (mg)	IE (%)	Corrosion Rate (mmpy × 10^{-2})
Mild steel			
Blank	34.5	-	8.0
ADIC	1.2	96.62	0.28
ADIP	1.3	96.25	0.30
ADIN	1.5	95.75	0.35
ADIS	1.8	94.87	0.42
Brass			
Blank	8.4	-	1.78
ADIC	1.0	88.26	0.21
ADIP	1.2	86.03	0.25
ADIN	1.8	78.77	0.38
ADIS	2.2	73.18	0.47
Copper			
Blank	5.7	-	1.16
ADIC	1.2	79.31	0.24
ADIP	1.5	74.13	0.30
ADIN	1.8	68.96	0.36
ADIS	2.4	58.62	0.49
Aluminum			
Blank	60.6	-	40.90
ADIC	10.6	82.51	7.15
ADIP	11.0	81.85	7.42
ADIN	11.3	81.36	7.62
ADIS	11.4	81.19	7.69

Table 3.3.6 Weight loss parameters obtained for 500 ppm concentration of 1-(2-aminoethyl)-2 undecyl-2-imidazoline salts at 40±1^{0}C and 90% relative humidity for 20 days for various metals

System	Weight loss (mg)	IE (%)	Corrosion Rate (mmpy × 10^{-2})
Mild steel			
Blank	34.5	-	8.0
AUIC	1.1	96.87	0.25
AUIP	1.9	94.25	0.44
AUIN	2.0	94.50	0.46
AUIM	3.4	96.87	0.79
Brass			
Blank	8.4	-	1.78
AUIC	0.6	93.44	0.12
AUIP	0.8	90.71	0.17
AUIN	1.3	85.24	0.27
AUIM	1.5	82.51	0.32
Copper			
Blank	5.7	-	1.16
AUIC	0.5	91.37	0.10
AUIP	0.6	89.65	0.12
AUIN	0.8	86.20	0.16
AUIM	1.0	82.75	0.20
Aluminum			
Blank	60.6	-	40.90
AUIC	11.7	80.70	7.89
AUIP	12.4	79.53	8.37
AUIN	12.7	79.04	8.57
AUIM	15.8	74.91	10.26

Table 3.3.7 Results obtained from Eschke test for ADIC at 40±1^{0}C and 90% relative humidity for 20 days for various metals

System	Visual observations	Corrosion Rate (mmpy × 10^{-2})
Mild steel (control)	Moderate to heavy rusting	0.460
ADIC	one to two rusted spots	0.080
Brass (control)	Moderate to heavy tarnishing	0.330
ADIC	Slight tarnishing	0.070
Copper (control)	Moderate to heavy tarnishing	0.280
ADIC	Slight tarnishing	0.030
Aluminum (control)	Heavy dulling, grayish white surface	6.22
ADIC	Slight dulling	1.78

Table 3.3.8 Results obtained from Eschke test for AUIC at 40±1^{0}C and 90% relative humidity for 20 days for various metals

System	Visual observations	Corrosion Rate (mmpy × 10^{-2})
Mild steel (control)	Moderate to heavy rusting	0.46
ADIC	1-2 rusted spots	0.06
Brass (control)	Moderate to heavy tarnishing	0.33
ADIC	Slight tarnishing	0.08
Copper (control)	Moderate to heavy tarnishing	0.28
ADIC	Slight tarnishing	0.07
Aluminum (control)	Heavy dulling, grayish white surface	6.26
ADIC	Slight dulling	1.96

Table 3.3.9 Results obtained from salt inoculation test for ADIC at 40±1^{0}C and 90% relative humidity for 20 days for various metals

System	Visual observations	Corrosion Rate (mmpy × 10^{-2})
Mild steel (control)	Whole surface covered with patches of brownish red spots	4.00
ADIC	Rusting restricted to nuclei, rest of suface bright and unattacked	2.90
Brass (control)	Rusting around nuclei	0.16
ADIC	Slight rusting around nuclei	0.07
Copper (control)	Rusting around nuclei	0.50
ADIC	Slight rusting around nuclei	0.40
Aluminum (control)	Moderate rusting around all nuclei, heavy dulling	5.90
ADIC	Rusting confined to nuclei, slight dulling	2.60

Table 3..3.10 Results obtained from salt inoculation test for AUIC at 40±1^{0}C and 90% relative humidity for 20 days for various metals

System	Visual observations	Corrosion Rate (mmpy × 10^{-2})
Mild steel (control)	Entire surface covered with patches of brownish red spots	4.00
AUIC	Corrosion restricted to nuclei, rest of suface bright and unattacked	1.90
Brass (control)	Corrosion around nuclei	0.16
AUIC	Slight corrosion around nuclei	0.042
Copper (control)	Corrosion around nuclei	0.50
AUIC	Slight corrosion around nuclei	0.16
Aluminum (control)	Moderate corrosion around all nuclei, heavy dulling	5.90
AUIC	Corrosion confined to nuclei, slight dulling	2.10

Table 3.3.11 Results obtained from SO_2 test for ADIC at 40±1^{0}C and 90% relative humidity for 24 hours for various metals

System	Visual observations	Corrosion Rate (mmpy × 10^{-2})
Mild steel (control)	Severely rusted all over surface	12.52
ADIC	No rusting, bright surface	0.90
Brass (control)	Moderate to heavy tarnishing	3.40
ADIC	Slight tarnishing	0.80
Copper (control)	Heavy tarnishing	2.40
ADIC	Slight tarnishing	0.80
Aluminum (control)	Slight dulling	5.40
ADIC	No effect, bright surface	1.30

Table 3.3.12 Results obtained from SO_2 test for AUIC at 40±1^{0}C and 90% relative humidity for 24 hours for various metals

System	Visual observations	Corrosion Rate (mmpy × 10^{-2})
Mild steel (control)	Severely rusted all over surface	12.52
AUIC	No rusting, bright surface	1.60
Brass (control)	Moderate to heavy tarnishing	3.40
AUIC	Slight tarnishing	0.80
Copper (control)	Heavy tarnishing	2.40
AUIC	Slight tarnishing	1.00
Aluminum (control)	Slight dulling	5.40
AUIC	No effect, bright surface	2.70

Table 3.3.13 Potentiodynamic polarization parameters obtained for 500 ppm concentration of 1-(2-aminoethyl)-2-dec-9- enyl-2-imidazoline salts at 28±2^{0}C for various metals

System	E_{corr} (mV)	I_{corr} (mA cm^{-2})	IE (%)
Mild steel			
Blank	−562	0.25	-
ADIC	−396	0.010	96.00
ADIP	−410	0.012	95.20
ADIN	−426	0.016	93.60
ADIS	−442	0.020	92.00
Brass			-
Blank	−340	0.20	
ADIC	−260	0.014	93.00
ADIP	−280	0.018	91.00
ADIN	−236	0.024	88.00
ADIS	−270	0.026	87.00
Copper			
Blank	−190	0.16	-
ADIC	−98	0.014	91.25
ADIP	−100	0.018	88.75
ADIN	−165	0.020	87.50
ADIS	−150	0.024	85.00
Aluminum			
Blank	−680	0.30	-
ADIC	−648	0.022	92.67
ADIP	−628	0.028	90.67
ADIN	−610	0.030	90.00
ADIS	−654	0.038	87.33

Table 3.3.14 Potentiodynamic polarization parameters obtained for 500 ppm concentration of 1-(2-aminoethyl)-2- undecyl-2-imidazoline salts at 28±2^{0}C for various metals

System	E_{corr} (mV)	I_{corr} (mA cm^{-2})	IE (%)
Mild steel			
Blank	−562	0.25	-
AUIC	−378	0.010	96.00
AUIP	−442	0.012	95.20
AUIN	−424	0.016	93.60
AUIM	−404	0.020	92.00
Brass			
Blank	−340	0.20	-
AUIC	−230	0.044	78.00
AUIP	−238	0.052	74.00
AUIN	−290	0.064	68.00
AUIM	−260	0.068	66.00
Copper			
Blank	−190	0.16	-
AUIC	−102	0.020	87.50
AUIP	−144	0.026	83.75
AUIN	−120	0.040	75.00
AUIM	−162	0.048	70.00
Aluminum			
Blank	−680	0.30	-
AUIC	−560	0.018	94.00
AUIP	−580	0.022	92.67
AUIN	−628	0.028	90.67
AUIM	−610	0.030	90.00

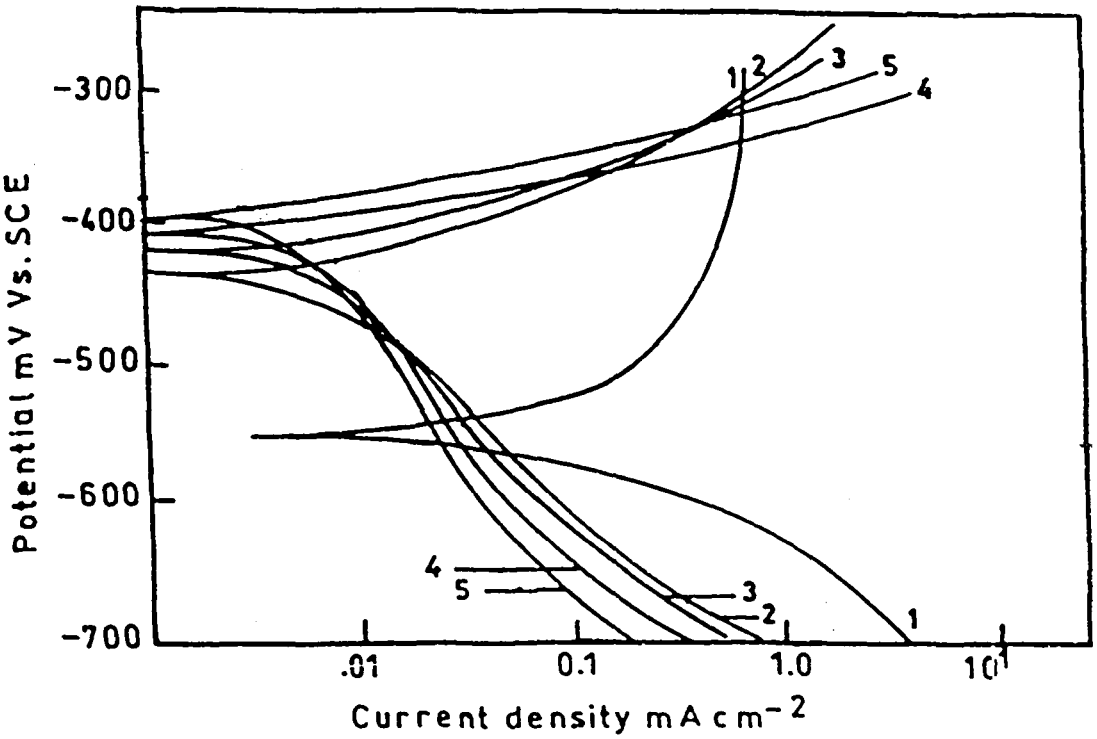


Figure 3.3.1A Potentiodynamic polarization curves for mild steel containing vapour phase corrosion inhibitors 1. Blank, 2. ADIS, 3. ADIN, 4. ADIP, 5. ADIC

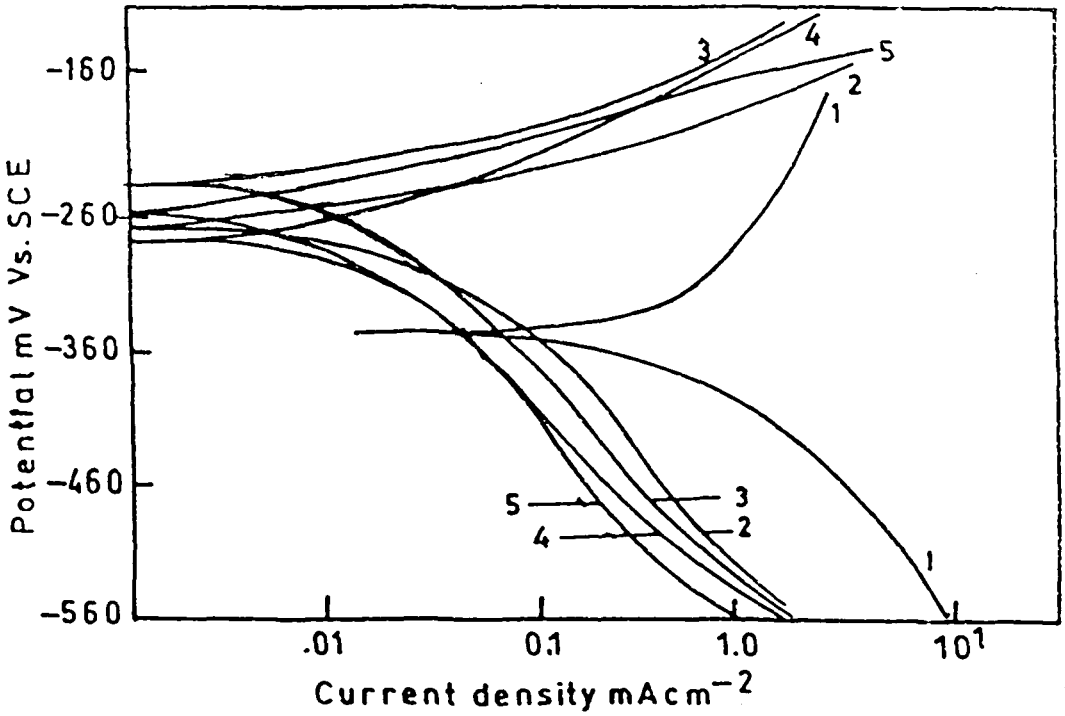


Figure 3.3.1B Potentiodynamic polarization curves for brass containing vapour phase corrosion inhibitors 1. Blank, 2. ADIS, 3. ADIN, 4. ADIP, 5. ADIC

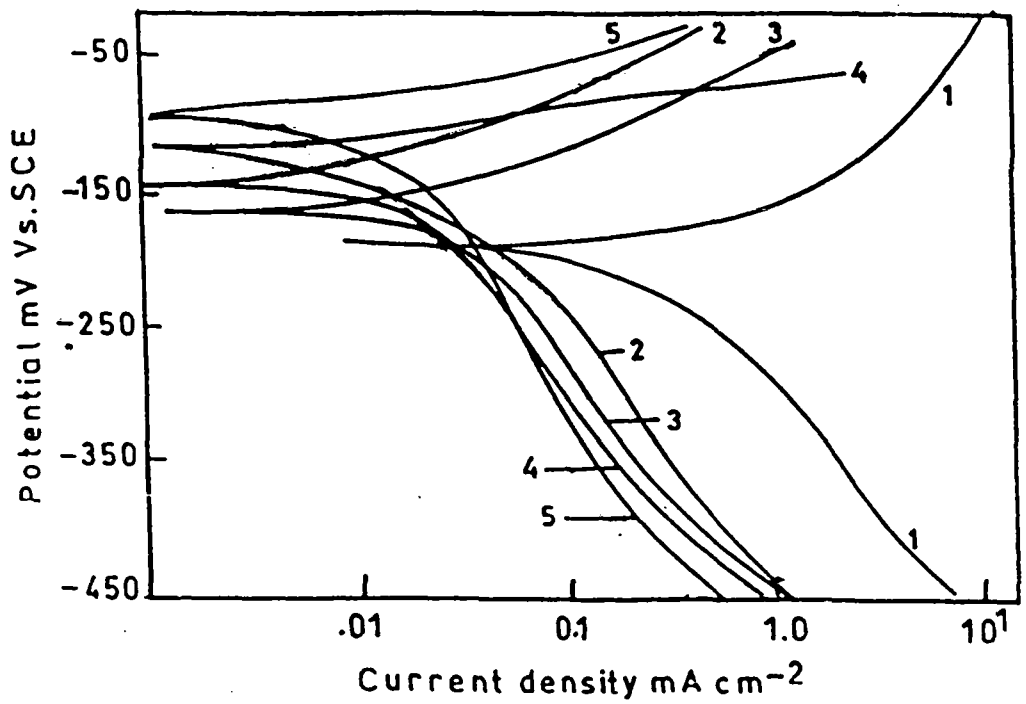


Figure 3.3.1C Potentiodynamic polarization curves for copper containing vapour phase corrosion inhibitors 1. Blank, 2. ADIS, 3. ADIN, 4. ADIP, 5. ADIC

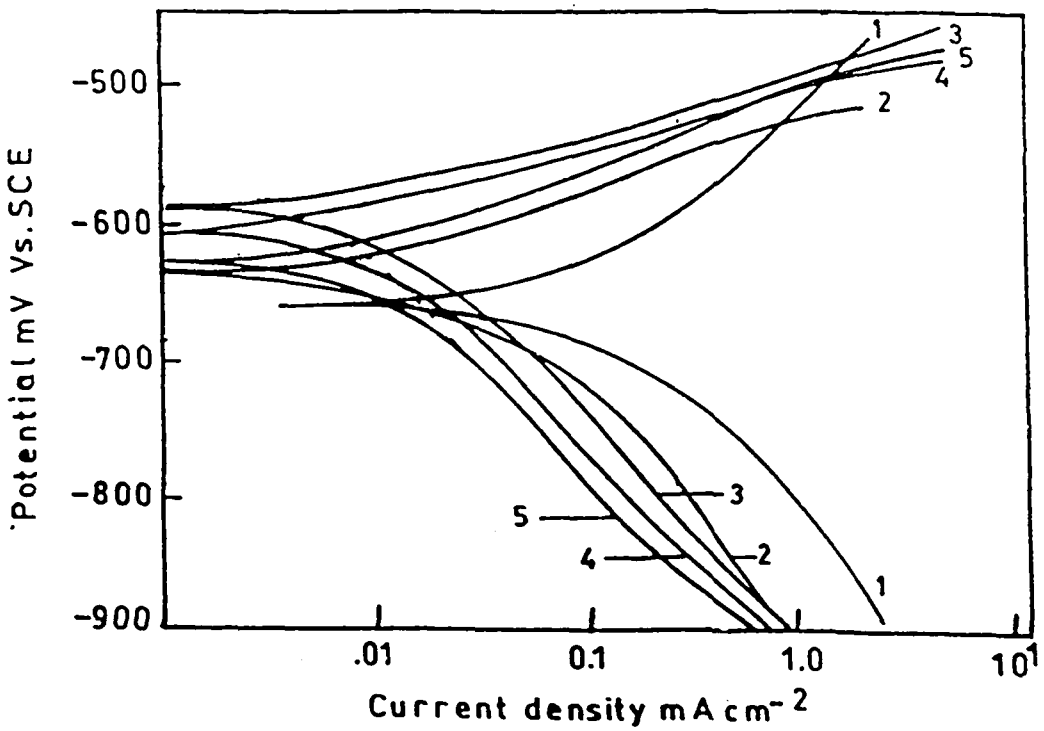


Figure 3.3.1D Potentiodynamic polarization curves for aluminum containing vapour phase corrosion inhibitors 1. Blank, 2. ADIS, 3. ADIN, 4. ADIP, 5. ADIC

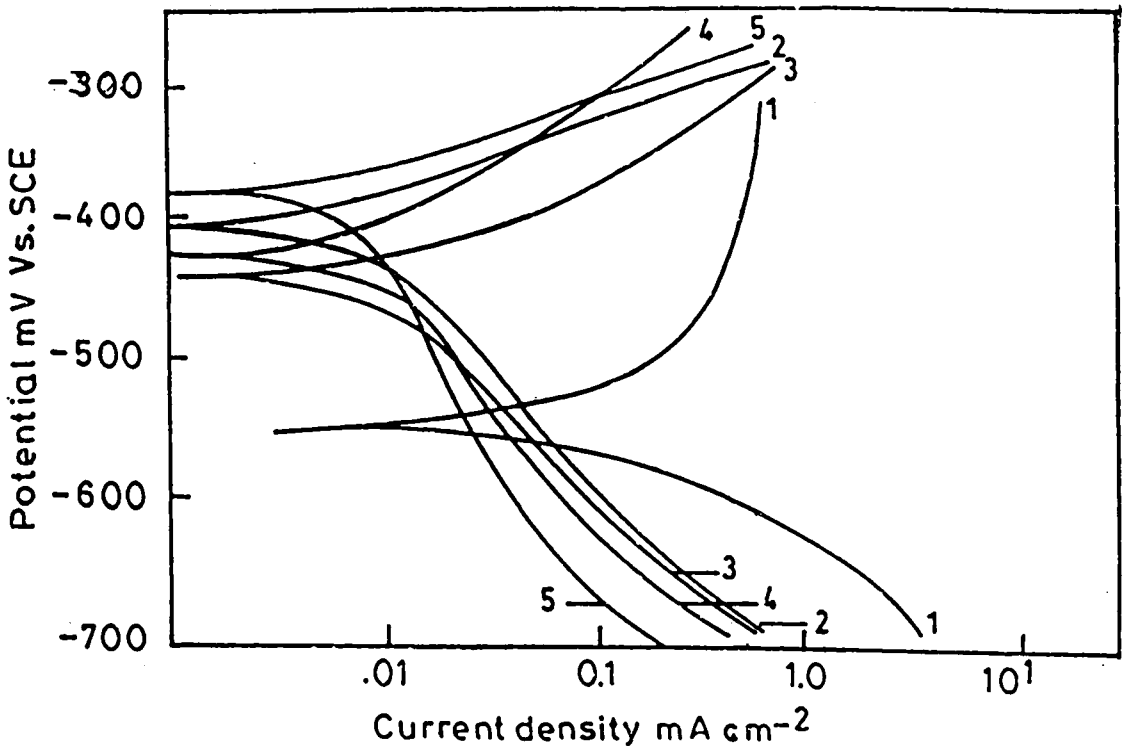


Figure 3.3.2A Potentiodynamic polarization curves for mild steel containing vapour phase corrosion inhibitors 1. Blank, 2. AUIM, 3. ADIN, 4. AUIP, 5. AUIC

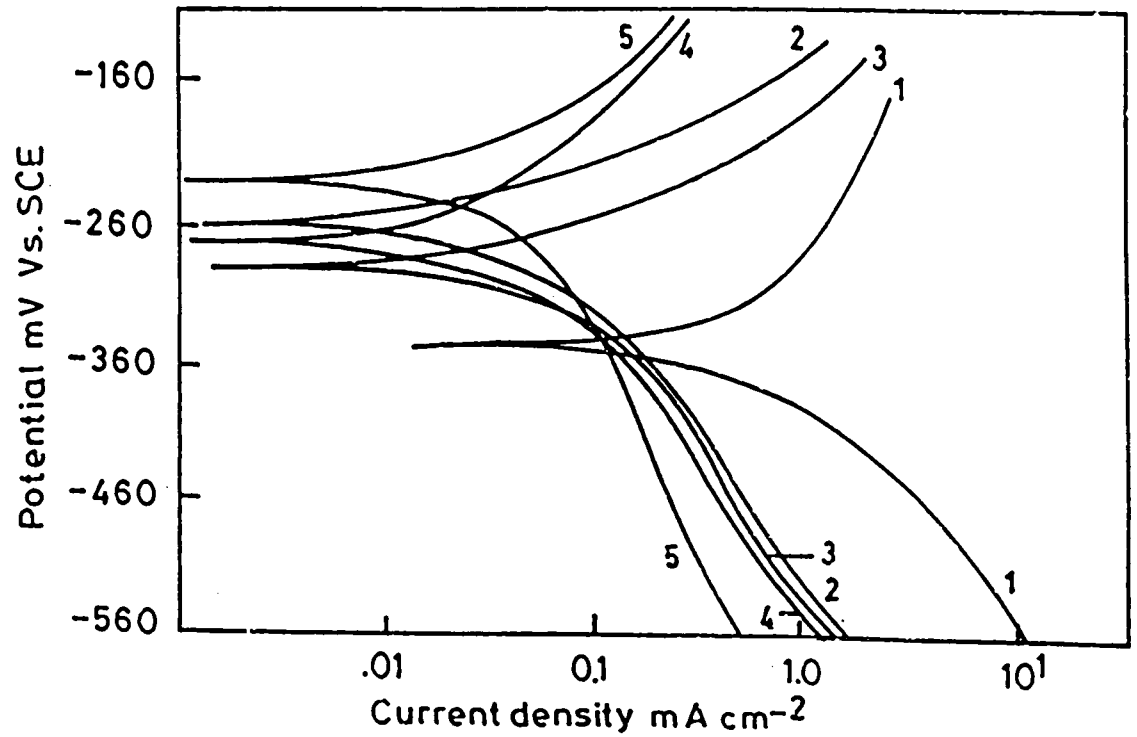


Figure 3.3.2B Potentiodynamic polarization curves for brass containing vapour phase corrosion inhibitors 1. Blank, 2. AUIM, 3. AUIN, 4. AUIP, 5. AUIC

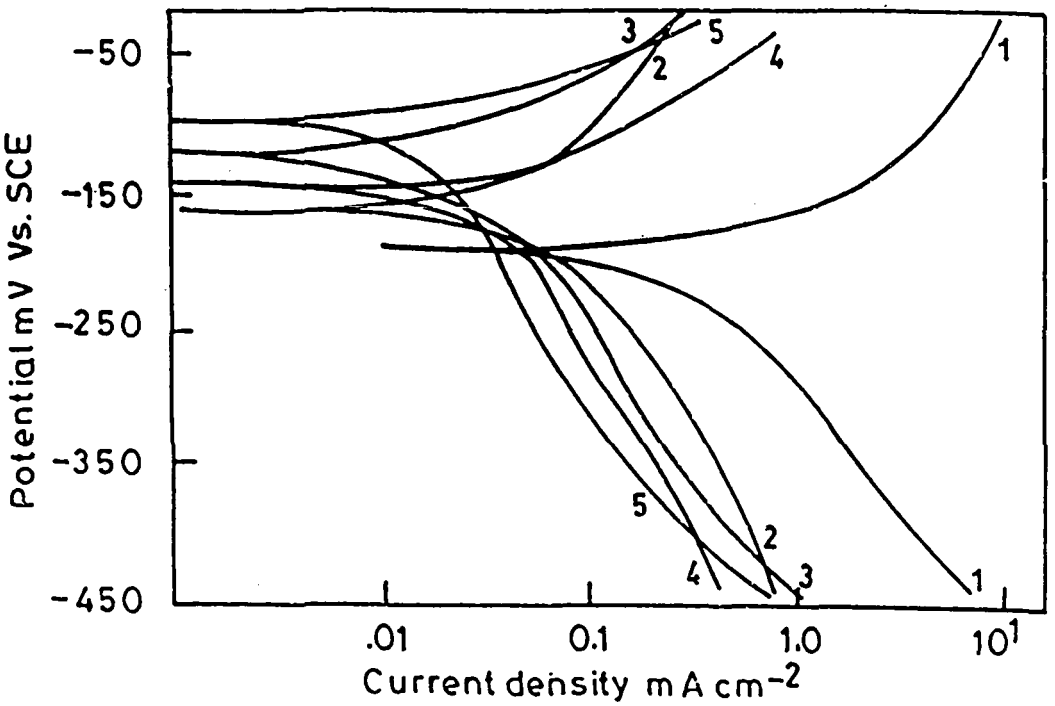


Figure 3.3.1C Potentiodynamic polarization curves for copper containing vapour phase corrosion inhibitors 1. Blank, 2. AUIM, 3. AUIN, 4. AUIP, 5. AUIC

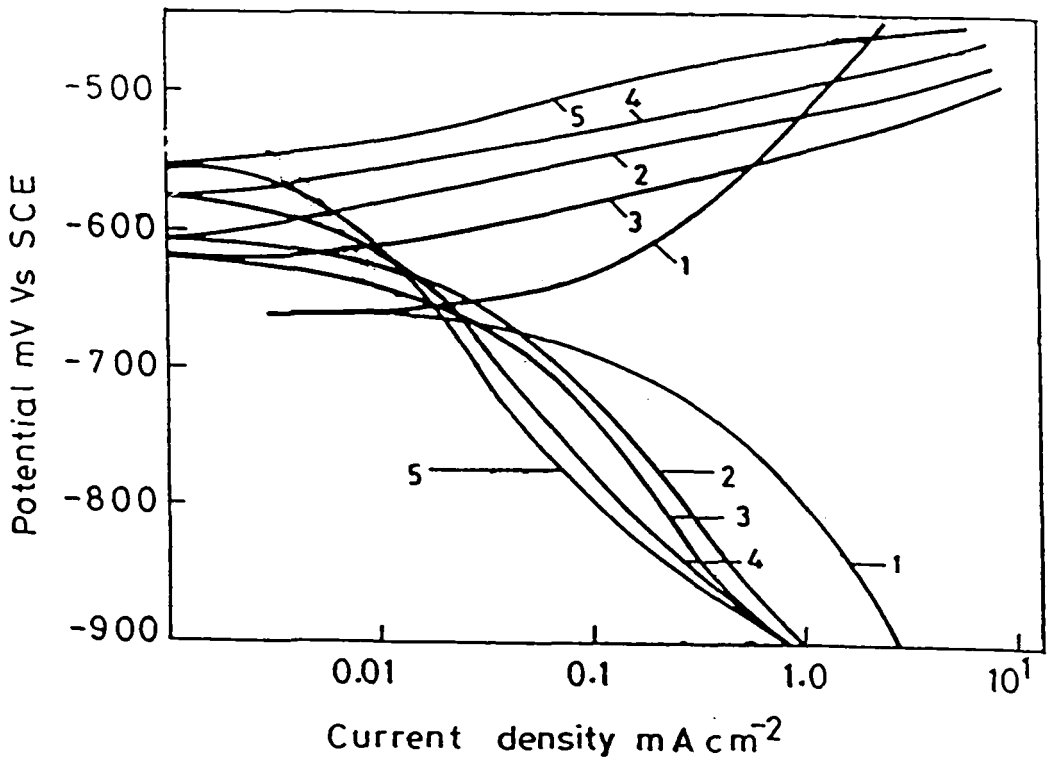


Figure 3.3.2D Potentiodynamic polarization curves for aluminum containing vapour phase corrosion inhibitors 1. Blank, 2. AUIM, 3. AUIN, 4. AUIP, 5. AUIC

3A.3.9 Conclusion

i. All the tested vapour phase corrosion inhibitors showed good inhibition efficiency for mild steel, brass and copper and aluminum.

ii. The cinnamate salts exhibited higher inhibition efficiency for all metals.

iii. All the organic compound showed effective vapour pressure.

iv. All the vapour phase corrosion inhibitors inhibited corrosion of metals by being adsorbed onto the metal surface.

v. All the compounds behaved as anodic type inhibitors.

Part – B

Corrosion Inhibition
by
Cooling Water Inhibitors

Section – 1

Triazole Derivatives
as
Corrosion Inhibitors for Brass

A survey of literature reveals that corrosion inhibitors derived from triazole and bezotriazole derivatives constitute an important and potential class of corrosion inhibitors for brass. Recently, Ravichandran et al. (19-21) studied corrosion behaviour of brass by some new bezotriazole derivatives in NaCl solution. Quraishi et al. (22,23) investgated influence of some new triazole derivatives of brass in NaCl solution.

Brass are usually used as components in cooling wter system. Studies on corrosion phenomenon of arsenic free 70/30 brass assume significance, as they are susceptible to corrosion phenomenon known as dezincification wherein selective dissolution of zinc occurs. This section of the chapter deals with the inhibitive action of two triazole derivatives on the dezincification of arsenic free 70/30 brass in 3.5% NaCl water. The performance of the triazole derivatives was evaluated using weight loss and potentiodynamic studies. Solution analysis was carried out to find the extent of dezincification.

3B.1.1 Corrosion Inhibitors

The molecular structure and other details of the compounds used as corrosion inhibitors are given in Table 3.4.1.

3B.1.2 Weight Loss Studies

The various parameters such as percentage inhibition efficieny (%I.E) and corrosion rate (C.R) of 70/30 brass in 3.5% NaCl water solution in absence and presence of ABMT and AHMT at different concentration at 50±1^{0}C are summarized in Table 3.4.2 . It has been observed inhibition efficiency for both compounds increase with increase in concentration. The maximum inhibition efficiency of each compound was achieved at 300 ppm. A further increase in the concentration of the compound does not causes any change in their performance.The order of inhibition was as follows :

ABMT > AHMT

The Inhibition efficiency of ABMT was more than that of AHMT. This may be attributed to higher inductive effect of butyl group in comparision to hydrizino

derivative The effectiveness of a given compounds as corrosion inhibitors depends on the structure of the organic compounds (9). The variation of inhibition efficiency mainly depends on the type and nature of the substituents present in the inhibitor(10).

3B.1.3 Potentiodynamic Polarization Studies

The cathodic and anodic polarization curves of brass in 3.5% NaCl water solution in presence and absence of ABMT and AHMT for different concentraion at 28±2 ^{0}C are shown in Figure 3.4.1 and figure 3.4.2 and various corrosion parameters such as E_{corr} , I_{corr} and %IE obtained from these curves are given in Table 3.4.3. It is observe that I_{corr} values decrease in the presence of ABMT and AHMT. The I_{corr} value for ABMT decseases more, indicating that ABMT is most effective corrosion inhibitor than AHMT. It has also been observed that both the triazole derivatives do not cause any appreciable change in E_{corr} value in the NaCl solution, thereby suggesting that both the inhibitors are of mixed type inhibitors.

Ravichandran et al. (19) recently studied polarization measurements showed that the organic cmpounds investigated as corrosion inhibitors in NaCl solution, are mixed type inhibitors, inhibiting the corrosion of brass by blocking the active sites of the metal surface.

3B.1.4 Solution Analysis

In order to asses the extent of dezincification, solution obtained in weight loss studies was analysed for copper and zinc by using atomic absorption spectroscopy (AAS).The results obtained from solution analysis are shown in Table 3.4.4. It is observed that preferential dissolution of zinc occured in absence of triazole derivatives. However, the dissolution of zinc decresed with increase in inhibitor concentration. At optimum concentration of inhibitors, the zinc concentration in solution was minimum. The results of this study indicate the effectivenss of triazole derivatives in inhibiting the dezincification of 70/30 brass.

Table 3.4.1 Name and structures of the compounds studied

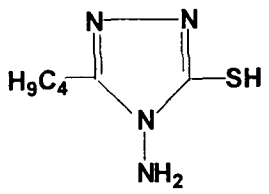
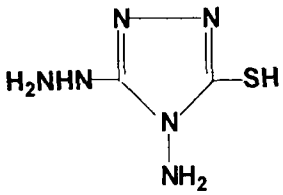
S.No.	Structure	Name and Abbreviation
1.		4-Amino-3 butyl-5-mercapto-1,2,4 triazole (ABMT)
2.		4-Amino-3 hydrazino-5-mercapto-1,2,4 triazole (AHMT)

Table 3.4.2 Weight loss parameters obtained for 70/30 brass in 3.5% NaCl in absence and presence of different concentration of ABMT and AHMT at 40±1^{0}C for 5 days

System	Weight loss (mg)	IE (%)	Corrosion Rate (mmpy × 10^{-2})
Blank	21.20	-	18.12
ABMT			
25	3.40	83.96	2.907
50	2.90	86.32	2.479
100	2.30	89.15	1.966
200	1.80	91.50	1.539
300	1.20	94.30	1.026
AHMT			
25	4.10	80.66	3.505
50	3.60	83.01	3.078
100	2.80	86.79	2.394
200	2.10	90.09	1.795
300	1.70	91.98	1.453

Table 3.4.3 Potentiodynamic polarization parameters obtained for 70/30 brass in 3.5% NaCl in containing optimum concentration of ABMT and AHMT at 28±2^{0}C for 5 days

System	E_{corr} (mV)	I_{corr} (μA cm^{-2})	IE (%)
Blank	−230	8.20	-
ABMT			
25	−230	1.60	80.48
100	−232	0.90	89.02
300	−236	0.50	93.90
AHMT			
25	−236	2.00	75.60
100	−234	1.50	81.70
300	−228	0.80	90.24

Table 3.4.4 Results of dezincification studies.

System	Solution Analysis (ppm)		Inhibition of dissolution (%)	
	Zn	**Cu**	**Zn**	**Cu**
Blank	3.362	0.010	-	-
ABMT				
25	0.920	0.00	72.60	100
50	0.634	0.00	81.40	100
100	0.426	0.00	87.30	100
200	0.396	0.00	88.22	100
300	0.350	0.00	89.60	100
AHMT				
25	1.068	0.00	68.20	100
50	0.862	0.00	75.43	100
100	0.510	0.00	84.80	100
200	0.442	0.00	86.80	100
300	0.436	0.00	87.03	100

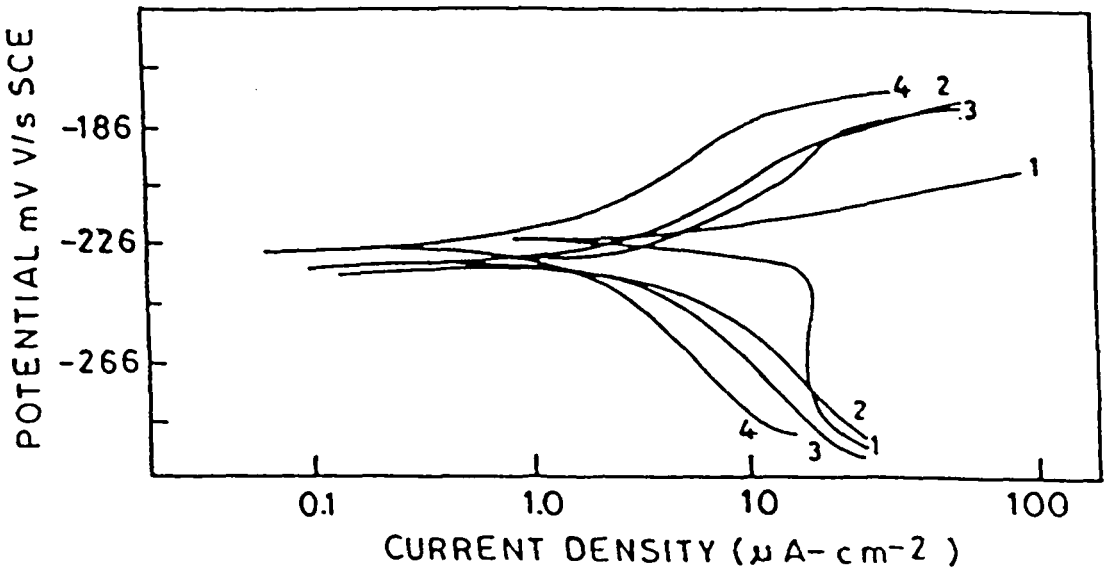


Figure 3.4.1 Potentiodynamic polarization curves for brass containing ABMT 1. Blank, 2. 25 ppm, 3. 100 ppm, 4. 300 ppm

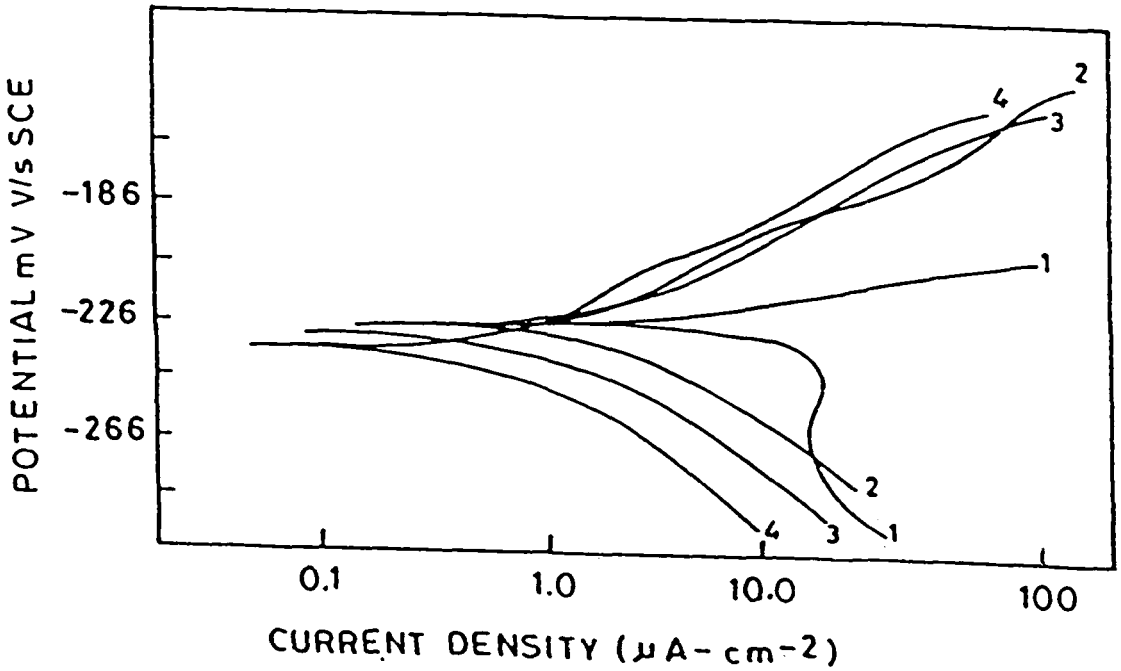


Figure 3.4.2 Potentiodynamic polarization curves for brass containing AHMT 1. Blank, 2. 25 ppm, 3. 100 ppm, 4. 300 ppm

3B.1.5 Conclusion

i. Both the triazole derivatives showed good inhibition efficiency for 70/30 brass in NaCl water solution..

ii. The inhibition efficiency of ABMT is higher than AHMT.

iii. The potentiodynamic polarization curves revealed that both the triazole derivatives are mixed type inhibitors.

iv. Solution analysis showed selective dissolution of zinc as compared with copper.

v. The lower concentration of zinc achieved with optimum inhibitor concentration.

Section – 2

Natural Products
as
Cooling Water Inhibitors for Mild Steel

Natural products with its cost effectiveness and availability has been used as potent corrosion inhibitors (24-29). Quraish et al. (30,31) studied some naturally occurring substances as corrosion inhibitors in sodium chloride solution.

This section of the chapter deals with the inhibitive action of the natural products as cooling water inhibitors on corrosion of mild steel in 3.5% NaCl water. The performance of the natural products was evaluated using weight loss and potentiodynamic studies. So

3B.2.1 Corrosion Inhibitors

Details of the compounds used as corrosion inhibitors are given in Table 3.5.1.

3B.2.2 Weight Loss Studies

The various parameters such as percentage inhibition efficieny (%I.E) and corrosion rate (C.R) of mild steel in 3.5% NaCl water solution in absence and presence of AS, AC and OB at different concentration at $50\pm1^{0}C$ are summarized in Table 3.5.2 . It has been observed inhibition efficiency for the compounds increase with increase in concentration. The maximum inhibition efficiency of each compound was achieved at optimum concentration. A further increase in the concentration of the compound does not causes any change in their performance. The order of inhibition was as follows :

$$AS > AC > OB$$

Aqueous extracts of the plant materials investigated in the present study were organic in nature, mostly sulphur, nitrogen and oxygen containing organic compounds. Adsorption of these constituents may occur through their sulphur, nitrogen and oxygen active centers. Furthermore, these compounds also may form complexes with the metallic cations. These complexes can cause blockage of microanodes and microcathoes that generated on the surface under of corrosive conditions and hence can retard the dissolution of metal.

3B.2.3 Potentiodynamic Polarization Studies

The cathodic and anodic polarization curves of mild steel in 3.5% NaCl water solution in presence and absence of AS, AC and OB at optimum concentration 3 ml/L at 28±2 ^{0}C are shown in Figure 3.5.1 and various corrosion parameters such as E_{corr} , I_{corr} and %IE obtained from these curves are given in Table 3.5.3. It is observe that I_{corr} values decrease in the presence of inhibitors. It has also been observed that all the compounds do not cause any appreciable change in E_{corr} value in the NaCl solution, thereby suggesting that all the inhibitors are of mixed type inhibitors.

Table 3.5.1 Organic contents of inhibitors studied

S.No.	Inhibitors	Abbreviation	Constituents
1.	Allium Sativum (garllic)	(AS)	Alliin, Allicin (diallylthiosulphide), diallyldisulphide
2.	Allium cepa (onion)	(AC)	Allyl propyl disulphide, Flavonides such as quercetin
3.	Ocimum basilcum (tulsi)	(OB)	Caffeic acid, tannins, beta carostenes

Table 3.5.2 Weight loss parameters obtained for mild steel in 3.5% NaCl in absence and presence of different concentration of AS, AC and OB at 50±1^{0}C for 5 days

System	Weight loss (mg)	IE (%)	Corrosion Rate (mmpy × 10^{-2})
Blank	92.3	-	85.65
AS(ml/L)			
1.0	33.50	63.70	31.08
2.0	30.90	66.52	28.52
3.0	28.40	69.23	26.21
AC(ml/L)			
1.0	45.30	47.00	41.53
2.0	40.90	55.68	37.75
3.0	35.80	61.21	33.22
OB(ml/L)			
1.0	58.20	34.10	53.71
2.0	52.10	43.55	48.08
3.0	48.90	47.02	45.13

Table 3.5.3 Potentiodynamic polarization parameters obtained for mild steel in 3.5% NaCl in containing optimum concentration of AS, AC and OB at 28±2^{0}C for 5 days

System	E_{corr} (mV)	I_{corr} (μA cm^{-2})	IE (%)
Blank	−550	20.0	-
AS	−570	7.00	65
AC	−565	8.00	60
OB	−568	10.0	50

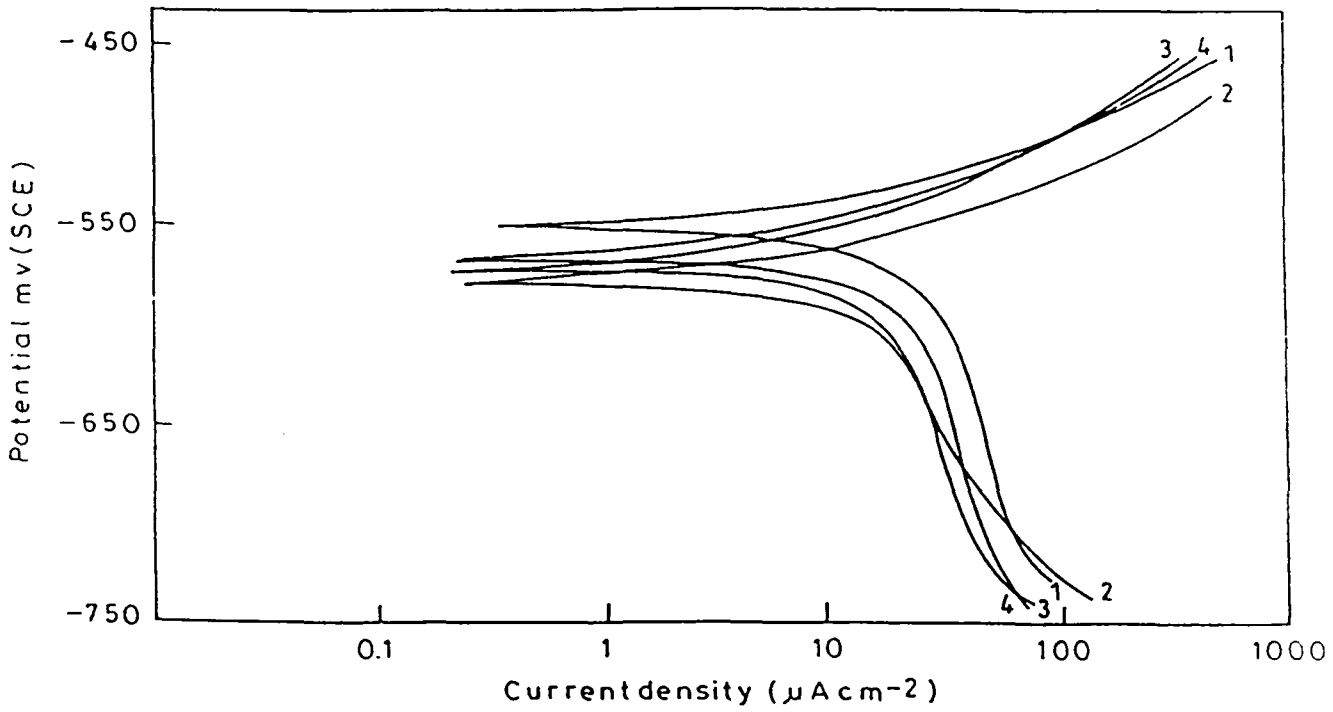


Figure 3.5.1 Potentiodynamic polarization curves for mild steel containing 1. Blank, 2. OB, 3. AC, 4. AS

3B.2.4 Conclusion

i. All the extract of plant material were found to inhibit corrosion of mild steel in NaCl water solution.

ii. The potentiodynamic polarization curves indicated that investigated extracts are mixed type inhibitors.

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LIST OF PUBLICATION

Published in Journals

1. Prevention of Metallic Corrosion by Lauric Hydrazide and its Salts under Vapor Phase Conditions.
   M. A. Quraishi, V.Bhardwaj and J. Rawat
   Journal of American Oil Chemist's Society (USA) Vol.79, No.6 2002, 603-609.

2. Development and Testing of New Volatile Corrosion Inhibitors for Multimetal Systems.
   M. A. Quraishi, D. Jamal and V. Bhardwaj
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3. Inhibition of Metallic Corrosion by Some 1-(2-aminoethyl)-2-undecyl-2 Imidazoline Salts under Vapour Phase Conditions.
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4. Protection of Metals by New Vapour Phase Corrosion Inhibitors.
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5. Prevention of Metallic Corrosion by Some Salts of Benzoic Hydrazide under Vapour Phase Conditions.
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Conference

1. Inhibition of Metallic Corrosion by Some 2-Cinnamyl Imidazoline Salts under Vapour Phase Conditions.
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Communicated

1. Inhibition of Metallic Corrosion by Schiff's bases under Vapour Phase Conditions
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2. Inhibiting Effect of Some Triazole Derivatives on 70-30 Brass Corrosion Process in NaCl Solution
   A. Mohammad, V. Bhardwaj and M. A. Quraishi

3. Investigation of Some Natural Products as Corrosion Inhibitors for Cooling Systems
   A. Mohammad, V. Bhardwaj and M. A. Quraishi

Prevention of Metallic Corrosion by Lauric Hydrazide and Its Salts Under Vapor Phase Conditions

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ABSTRACT: Six organic volatile corrosion inhibitors (VCI) were synthesized using lauric hydrazide with various acids such as cinnamic acid, succinic acid, nitrobenzoic acid, phthalic acid, and maleic acid and evaluated as corrosion inhibitors of mild steel, copper, brass, zinc, and aluminum by weight loss and potentiodynamic polarization methods. All the investigated VCI exhibited good inhibition efficiency for all the metals tested. The inhibition efficiency of all compounds increased as the inhibitor concentration increased. Lauric hydrazide cinnamate showed the best results among all compounds studied. In addition, all inhibitors showed anodic behavior. Adsorption studies demonstrated that all the investigated compounds followed Temkin's adsorption isotherm.

Paper no. J10089 in *JAOCS 79*, 603–609 (June 2002).

KEY WORDS: Ferrous and nonferrous metals, lauric hydrazide, potentiodynamic polarization, Temkin's adsorption isotherm, volatile corrosion inhibitor.

Corrosion is defined as the destruction or deterioration of metals by chemical means in environments to which they are exposed (1). Corrosion causes enormous economic losses. In the United States, the economic losses have been estimated as high as $270 billion per year. Corrosion of metal surfaces commonly occurs in the presence of oxygen and moisture and involves electrochemical reactions. Oxidation takes place at anodic sites and reduction occurs at cathodic sites. In an acidic medium, a hydrogen evolution reaction predominates, whereas in a neutral medium, reduction of oxygen takes place.

Corrosion inhibitors reduce or prevent these reactions. They are adsorbed onto the metal surface and act by forming a barrier to oxygen and moisture, by complexing with metal ions or by removing corrodants from the environment. Some of the inhibitors facilitate formation of a passivating film on the metal surface.

Volatile corrosion inhibitors (VCI) are used to protect metallic articles and equipment in an enclosed atmosphere (2). The choice of a chemical compound as a vapor phase VCI depends on its vapor pressure as well as its efficiency in preventing corrosion by forming a protective film. Numerous investigations of corrosion inhibition have utilized aliphatic amines, alicyclic amines, and their salts as VCI for various industrial metals and alloys (3–5). FA amines were more effective than cyclic amines and aromatic amines (5). *m*-Dinitrobenzene with β-naphthol was examined as a VCI in a SO_2 and chloride atmosphere by Rajagopalan *et al.* (6). Subramanian *et al.* (7) studied the corrosion-inhibiting performance of cyclohexylamine salts and dicyclohexylamine salts on copper, mild steel, and zinc in an SO_2 environment. Dicyclohexylamine exhibited 70.86, 85.15, and 91.81% inhibition efficiency (IE) in mild steel, copper and zinc, respectively. Subramanian *et al.* (8) recently studied the corrosion-inhibiting behavior of morpholine and its three salts, i.e., morpholine carbonate, borate, and phosphate salts. Of these, morpholine and its carbonate salt exhibited 90 and 85% IE, respectively, whereas the other salts showed less than 40% IE.

Continuing our recent work (9–10) on FA derivatives as corrosion inhibitors, we report here the inhibiting properties of six organic vapor VCI, namely, lauric hydrazide (LH), lauric hydrazide cinnamate (LHC), lauric hydrazide nitrobenzoate (LHNB), lauric hydrazide maleate (LHM), lauric hydrazide succinate (LHS), and lauric hydrazide phthalate (LHP) on mild steel, brass, copper, aluminum, and zinc.

MATERIALS AND METHODS

Weight loss measurements. Corrosion experiments were carried out using various ferrous and nonferrous metals, *viz.*, mild steel, brass, copper, aluminum, and zinc. Specimens of size 2.0 × 2.0 × 0.025 cm were used for weight loss measurement studies. Weight loss experiments were carried out in the presence and absence of inhibitors at concentrations ranging from 250–1000 ppm, using tight-fitting rubber-corked jars containing 25 mL of water. Concentrations of the inhibitors were taken according to the volume of the jar. Metal specimens were suspended in these bottles with nylon tags and just below these specimens, weighed VCI samples were kept in a glass container, to avoid contact with the liquid kept inside the jar, at a temperature of 35 ± 1°C for 30 d. Relative humidity was kept at 100% to allow continuous condensation of moisture on the metal specimen.

Synthesis of inhibitors. LH was synthesized according to the procedure reported in the literature (11), and the salts were prepared by dissolving equimolar amounts of LH and organic acids in ethanol. The reaction mixture was stirred for 1.0 h at 40°C, and the precipitated compounds were filtered and crystallized from ethanol. Melting points (in °C) of the salts were as follows: LH = 85, LHC = 120, LHNB = 130, LHP = 135,

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Serial no.	Molecular structure	Name	Vapor pressure (Pa)
1	$CH_3\text{-}(CH_2)_{10}\text{-}C(=O)\text{-}NHNH_2$	Lauric hydrazide (LH)	1.87×10^{-4}
2	$CH_3\text{-}(CH_2)_{10}\text{-}C(=O)\text{-}NHNH_2\text{-}HOOC\text{-}CH{=}CH$–C$_6H_5$	Lauric hydrazide cinnamate (LHC)	0.80×10^{-4}
3	$CH_3\text{-}(CH_2)_{10}\text{-}C(=O)\text{-}NHNH_2\text{-}HOOC$–C$_6H_4$–$NO_2$	Lauric hydrazide nitrobenzoate (LHNB)	1.23×10^{-4}
4	$CH_3\text{-}(CH_2)_{10}\text{-}C(=O)\text{-}NHNH_2\text{-}HOOC$–C$_6H_4$–COOH	Lauric hydrazide phthalate (LHP)	1.04×10^{-4}
5	$CH_3\text{-}(CH_2)_{10}\text{-}C(=O)\text{-}NHNH_2\text{-}HOOC\text{-}CH{=}CHCOOH$	Lauric hydrazide maleate (LHM)	1.54×10^{-4}
6	$CH_3\text{-}(CH_2)_{10}\text{-}C(=O)\text{-}NHNH_2\text{-}HOOC\text{-}CH_2\text{-}CH_2\text{-}COOH$	Lauric hydrazide succinate (LHS)	1.18×10^{-4}

LHM = 115, and LHS = 140. Names and molecular structures of these compounds are presented in Table 1.

Potentiodynamic polarization studies. For potentiodynamic polarization studies, metal strips without inhibitor and those with a 500 ppm concentration of inhibitor were embedded in araldite (a fixing material, made up of epoxy resin; Aldrich Chemical Co., St. Louis, MO) with an exposed area of 1.0 cm^2. Potentiodynamic polarization studies were carried out at a constant temperature of 28 ± 2°C according to ASTM methods G 3-74 and G 5-87 (12) using a potentiostat/galvanostat (model 173; EG&G, Gaithersburg, MD), a universal programmer (model 175, EG&G), and an X-Y recorder (model RE 0089; EG&G). A platinum foil was used as the auxiliary electrode and a saturated calomel electrode served as reference. Analyzed reagent-grade sodium sulfate (Na_2SO_4) (Merck) and double-distilled water were used for preparing test solutions of 1 N Na_2SO_4 for all experiments, which were used as electrolyte solutions.

Eschke test. Corrosion tests also were carried out according to the procedure reported in the literature (13) using mild steel, brass, copper, aluminum, and zinc. Polished strips of size 5.0 × 2.0 × 0.25 cm were wrapped in a single layer of inhibitor-impregnated kraft paper and suspended in a climatic cabinet maintained at 90% relative humidity. One gram per square foot of each inhibitor was used for the experiment. The temperature cycle was set at 40°C for 12 h and at room temperature for another 12 h for condensation of the moisture. The duration of the test was 20 d. A similar experiment was done with metals covered with untreated kraft paper (control).

Determination of vapor pressure of the inhibitors. The weighed compound was placed in a glass container with a hole of 1.0 mm in diameter. The glass container was then placed in an oven set at 35°C for 30 d. Loss in mass was measured, and the values were substituted into the formula given below (14):

$$p = \frac{W}{At} \times \left(\frac{2\pi RT}{M}\right)^{1/2} \quad [1]$$

where p = vapor pressure of the inhibitor, A = area of the hole in m^2, t = time in seconds, W = mass loss in kilograms, T = temperature in Kelvin, M = molecular mass of the compound, and R = gas constant (8.314 J K^{-1} mol^{-1}). Values of the vapor pressures obtained are given in Table 1.

RESULTS AND DISCUSSION

Weight loss measurements. The values of IE values and corrosion rates obtained by weight loss methods at different LH salt concentrations at 35 ± 1°C are summarized in Table 2. IE and surface coverage (θ) were calculated using the following equations:

$$\%\ IE = \left[\left(W^0 - W\right)/W^0\right] \times 100 \quad [2]$$

$$\theta = \left[\left(W^0 - W\right)/W^0\right] \quad [3]$$

where W^0 and W are the weight loss in the absence and presence of inhibitors, respectively. Table 2 indicates the increase in IE with increasing inhibitor concentration. The IE was obtained at 1,000 ppm. All VCI showed good IE, which may be attributed to the formation of a physical barrier between the metal and corrosive environment by the interaction of metal and inhibitor molecules. However, the difference in their inhibiting action can be explained by their molecular structure.

The corrosion-inhibiting action of LH is attributed to the

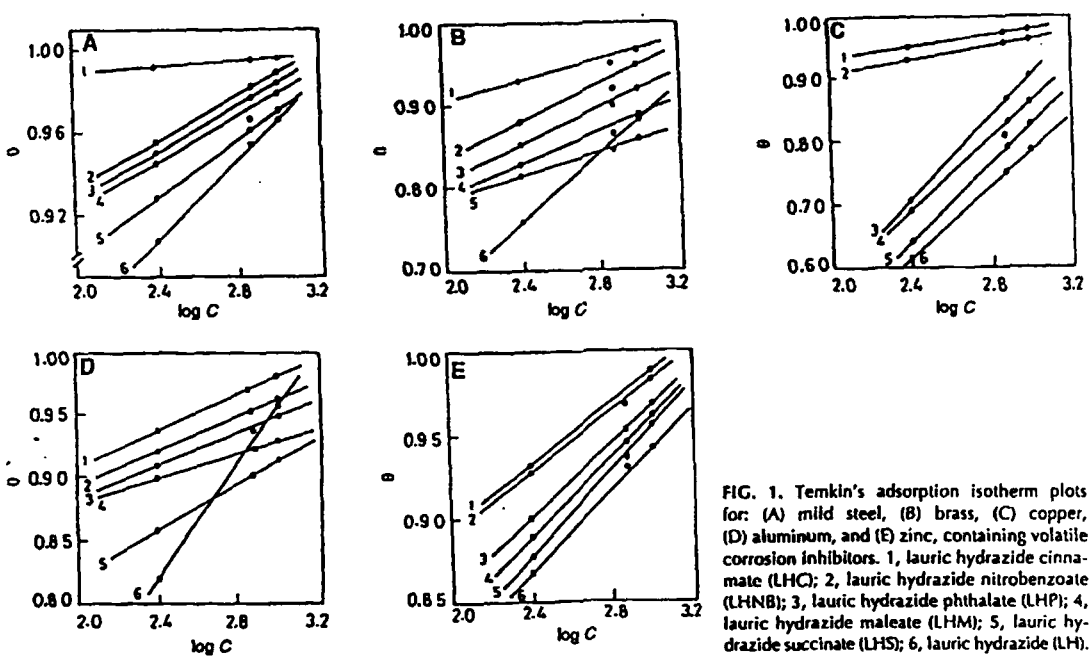

FIG. 1. Temkin's adsorption isotherm plots for: (A) mild steel, (B) brass, (C) copper, (D) aluminum, and (E) zinc, containing volatile corrosion inhibitors. 1, lauric hydrazide cinnamate (LHC); 2, lauric hydrazide nitrobenzoate (LHNB); 3, lauric hydrazide phthalate (LHP); 4, lauric hydrazide maleate (LHM); 5, lauric hydrazide succinate (LHS); 6, lauric hydrazide (LH).

presence of a lone pair of electrons on the N atom of the molecule that facilitates adsorption of inhibitor molecules on the metal surface. In the present investigation, the LHC salt exhibited good performance as a corrosion inhibitor owing to the presence of an additional π-bond between carbon atoms (–C=C–) which facilitates greater adsorption of cinnamate onto the metal surface, thereby giving high IE (16). The corrosion-inhibiting action of the LHNB is attributed to the presence of a nitro group. LHP showed better IE than the the LHM or LHS salts owing to the presence of an additional aromatic ring in the molecule. The inhibitive action of LHM is attributed to the presence of a double bond between the –C=C– atoms through which they adsorb strongly onto the surface of metals.

The degree of surface coverage (θ) for different inhibitor concentrations has been evaluated from weight loss values. The data were tested graphically by fitting to various isotherms. A straight line was obtained on plotting θ vs. log C (Figs. 1A–E), suggesting that the adsorption of LH salts onto the metal surface occurred according to Temkin's adsorption isotherm.

Eschke test. Visual observations of the metal specimens of this test are summarized in Table 3. The IE values and corrosion rates obtained in the presence and absence of various inhibitors are also summarized in Table 3.

Potentiodynamic polarization studies. Potentiodynamic polarization studies were carried out by immersing metal coupons and inhibited coupons in a 1 N Na_2SO_4 solution. The corrosion parameters, such as corrosion current density (I_{corr}), corrosion potential (E_{corr}), and percentage of IE (% IE) obtained from the potentiodynamic polarization curves are given in Table 2. The I_{corr} value was found to decrease significantly in the presence of the inhibitors, indicating that the compounds were effective corrosion inhibitors. All of these compounds shifted the E_{corr} in a more positive direction, suggesting that they were predominantly anodic inhibitors. Fiures 2A–E show the Tafel plots obtained from different inhibited coupons in the presence of the 1 N Na_2SO_4 electrolyte solution for mild steel, brass, copper, aluminum, and zinc.

Mechanism of corrosion inhibition. Inhibition of metallic corrosion in the presence of LH salts involves vaporization of the inhibitor in a nondissociated molecular form, followed by hydrolysis of the salts into carboxylate anions ($RCOO^-$) and organic cations ($RCONHNH_3^+$). Anions are adsorbed onto the anodic site of the metal and inhibit anodic reaction, whereas organic cations are adsorbed onto the cathodic site, thereby preventing cathodic reaction (17).

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TABLE 2
Weight Loss Parameters and Electrochemical Parameters Obtained from Different Vapor Phase VCI Concentrations at 40°C and 100% Humidity for 30 d for Mild Steel, Brass, Copper, Aluminum, and Zinc[a]

Inhibitor concentration (ppm)	Weight loss studies			Electrochemical studies		
	Weight loss (mg)	IE (%)	CR (mmpy x 10^{-2})	E_{corr} (mV)	I_{corr} (mA cm^2)	IE (%)
Mild steel						
Blank	38.5	—	5.95	−562	0.25	—
LH						
250	3.6	90.65	0.557	−448	0.042	83.20
750	1.8	95.32	0.279	−458	0.036	85.60
1,000	1.2	96.88	0.186	−430	0.032	87.20
LHC						
250	0.3	99.22	0.464	−426	0.014	94.40
750	0.2	99.48	0.310	−444	0.012	95.20
1,000	0.1	99.74	0.155	−416	0.008	96.80
LHNB						
250	1.7	95.58	2.63	−432	0.022	91.20
750	0.7	98.28	1.08	−428	0.018	92.80
1,000	0.4	98.96	0.62	−408	0.010	96.00
LHP						
250	1.9	95.06	2.94	−432	0.024	90.40
750	1.0	97.40	1.55	−446	0.022	91.20
1,000	0.6	98.44	1.29	−450	0.018	92.80
LHM						
250	2.1	94.54	3.25	−458	0.038	84.80
750	1.4	96.36	2.16	−464	0.030	88.00
1,000	0.8	97.14	1.24	−488	0.020	92.00
LHS						
250	2.8	92.73	4.33	−466	0.040	84.00
750	1.5	96.10	2.30	−446	0.034	86.40
1,000	1.1	97.14	1.70	−480	0.026	89.60
Brass						
Blank	12.0	—	1.72	−340	0.20	—
LH						
250	2.8	76.67	0.402	−290	0.050	75.00
750	1.6	86.33	0.230	−300	0.036	82.00
1,000	1.4	88.33	0.201	−270	0.026	87.00
LHC						
250	0.8	93.33	0.115	−260	0.020	90.00
750	0.6	95.00	0.086	−250	0.018	91.00
1,000	0.3	97.50	0.043	−222	0.010	95.00
LHNB						
250	1.4	88.33	0.201	−256	0.026	87.00
750	0.9	92.50	0.129	−254	0.024	88.64
1,000	0.5	95.83	0.718	−250	0.016	90.00
LHP						
250	2.0	83.33	0.287	−240	0.030	85.00
750	1.7	88.40	0.244	−252	0.022	89.00
1,000	0.7	89.20	0.101	−260	0.014	93.00
LHM						
250	1.8	85.00	0.259	−264	0.038	81.00
750	1.2	90.00	0.172	−270	0.028	86.00
1,000	0.9	92.50	0.129	−280	0.018	91.00
LHS						
250	2.1	82.53	0.302	−250	0.040	80.00
750	1.9	84.17	0.273	−240	0.032	84.00
1,000	1.2	86.74	0.172	−236	0.024	88.00
Copper						
Blank	9.7	—	1.317	−190	0.16	—
LH						
250	3.8	60.82	0.516	−160	0.048	70.00
750	2.7	72.16	0.367	−166	0.032	80.00
1,000	2.0	79.38	0.272	−150	0.024	85.00
LHC						
250	0.4	95.88	0.054	−140	0.028	82.50
750	0.3	96.90	0.041	−150	0.020	87.50
1,000	0.1	98.97	0.014	−112	0.012	92.50
LHNB						
250	0.6	93.81	0.081	−122	0.030	81.25
750	0.4	95.88	0.054	−138	0.024	85.00
1,000	0.2	97.94	0.027	−98	0.014	91.25

TABLE 2 (continued)

Inhibitor concentration (ppm)	Weight loss studies			Electrochemical studies		
	Weight loss (mg)	IE (%)	CR (mmpy × 10^{-2})	E_{corr} (mV)	I_{corr} (mA cm^2)	IE (%)
LHP						
250	2.8	71.13	0.338	−120	0.034	74.56
750	1.3	83.51	0.176	−122	0.032	80.00
1,000	0.8	91.75	0.109	−124	0.024	85.00
LHM						
250	3.0	69.07	0.407	−140	0.036	77.50
750	1.8	81.44	0.244	−136	0.024	85.00
1,000	1.2	87.63	0.163	−100	0.018	88.75
LHS						
250	3.4	64.95	0.462	−170	0.040	75.00
750	2.0	79.38	0.272	−160	0.032	80.00
1,000	1.6	83.51	0.217	−165	0.020	87.50
Aluminum						
Blank	60.6	—	27.30	−680	0.30	—
LH						
250	7.8	87.12	3.51	−640	0.050	83.33
750	4.1	93.23	1.85	−630	0.040	86.67
1,000	3.5	94.22	1.58	−654	0.038	87.33
LHC						
250	3.8	93.73	1.71	−610	0.028	90.67
750	1.4	97.69	0.631	−600	0.022	92.67
1,000	0.8	98.68	0.360	−595	0.018	94.00
LHNB						
250	4.2	93.07	1.89	−646	0.036	88.00
750	1.8	97.03	0.81	−638	0.028	90.67
1,000	1.2	98.02	0.541	−648	0.022	92.67
LHP						
250	5.8	90.43	2.61	−650	0.034	90.00
750	3.0	95.02	1.35	−646	0.030	92.68
1,000	1.6	97.36	0.721	−640	0.020	96.60
LHM						
250	6.4	89.44	2.88	−650	0.044	85.33
750	3.4	94.39	1.80	−640	0.038	87.33
1,000	2.1	96.53	0.946	−628	0.028	90.67
LHS						
250	7.0	88.45	3.15	−666	0.048	84.00
750	3.7	93.89	1.67	−642	0.040	86.67
1,000	2.2	96.37	0.991	−610	0.030	90.00
Zinc						
Blank	78.9	—	134.64	−708	0.38	—
LH						
250	14.0	82.26	2.39	−680	0.058	84.74
750	5.5	93.03	0.939	−676	0.048	87.37
1,000	3.2	95.94	0.546	−682	0.044	88.42
LHC						
250	4.5	94.30	0.768	−640	0.038	90.00
750	2.2	97.21	0.375	−632	0.026	93.16
1,000	1.5	98.10	0.256	−616	0.020	94.74
LHNB						
250	5.9	92.52	1.01	−658	0.042	88.95
750	3.8	95.10	0.648	−640	0.036	90.53
1,000	3.0	96.20	0.512	−638	0.024	93.68
LHP						
250	6.4	91.80	1.09	−666	0.048	87.37
750	5.6	93.36	0.956	−650	0.040	89.47
1,000	3.5	95.56	0.597	−640	0.030	92.68
LHM						
250	6.9	91.25	1.18	−688	0.048	87.37
750	5.8	92.65	0.990	−672	0.038	90.00
1,000	5.5	93.03	0.939	−670	0.028	92.63
LHS						
250	10.7	86.44	1.83	−680	0.050	86.84
750	7.2	90.87	1.23	−660	0.040	89.47
1,000	5.4	93.16	0.921	−652	0.032	91.58

[a]IE, inhibition efficiency; CR, corrosion rate; E_{corr}, corrosion potential; I_{corr}, corrosion current density. For other abbreviations see Table 1.

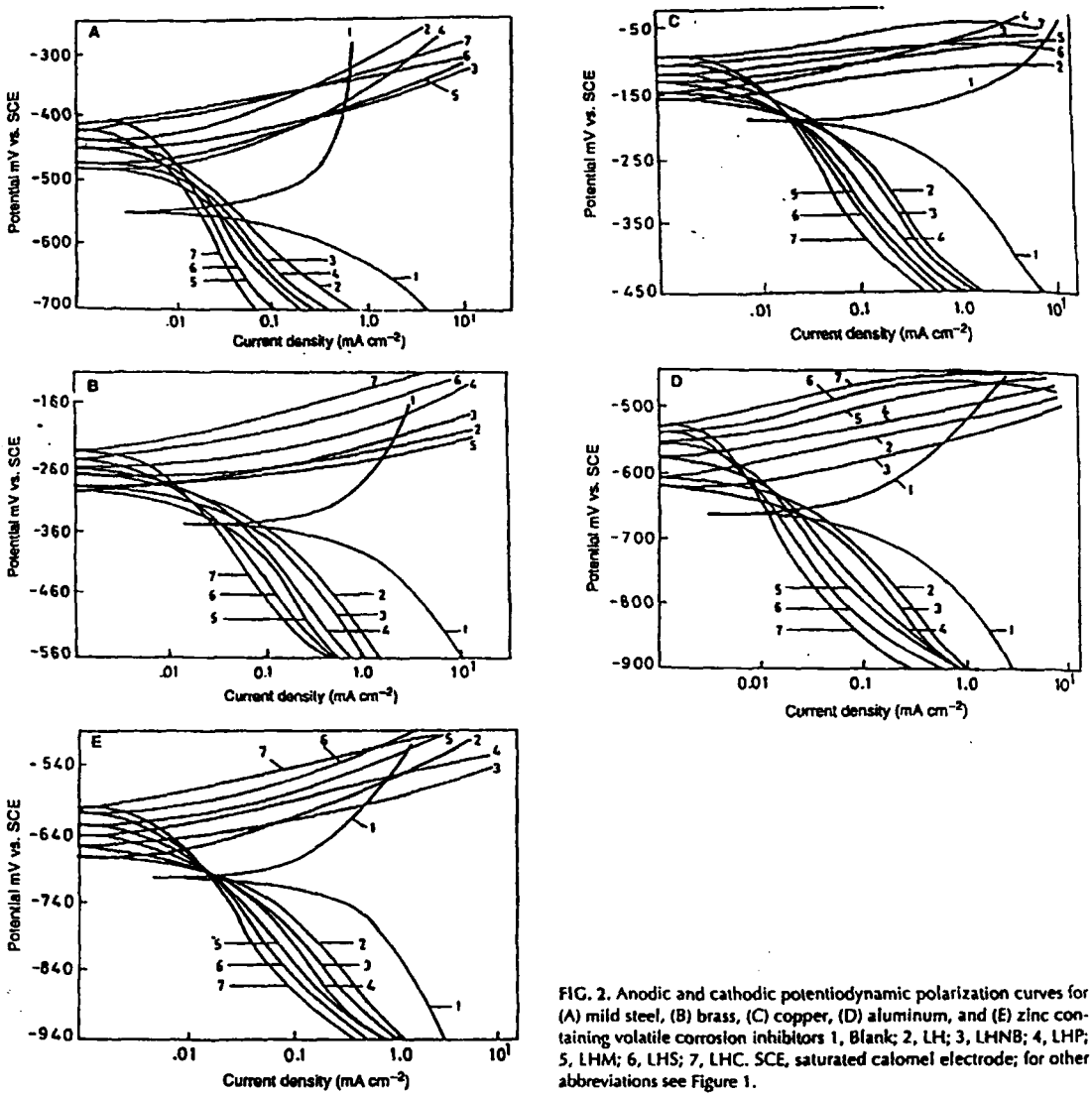

FIG. 2. Anodic and cathodic potentiodynamic polarization curves for (A) mild steel, (B) brass, (C) copper, (D) aluminum, and (E) zinc containing volatile corrosion inhibitors 1, Blank; 2, LH; 3, LHNB; 4, LHP; 5, LHM; 6, LHS; 7, LHC. SCE, saturated calomel electrode; for other abbreviations see Figure 1.

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TABLE 3
Results Obtained from the Eschke Test[a]

Metal	VCI	Extent of corrosion	Surface layer color	IE (%)	CR (mmpy $\times 10^{-3}$)
Mild steel	Control	High	Brownish-red	—	3.22
	LH	Moderate	Blackish-grey	90.38	0.31
	LHC	Very low	Dull white	96.15	0.12
Brass	Control	High	Yellowish-brown	—	1.35
	LH	Low	Dull yellow	82.98	0.23
	LHC	Very low	Yellow	96.43	0.13
Copper	Control	High	Reddish-brown	—	1.06
	LH	Moderate	Yellowish-brown	87.18	0.14
	LHC	Very low	Yellowish-brown	91.03	1.00
Bronze	Control	High	Deep brown	—	1.12
	LH	Low	Light brown	85.37	0.16
	LHC	Very low	Yellowish-brown	90.24	0.11
Aluminum	Control	High	Grayish-white	—	16.40
	LH	Moderate	Dull white	87.80	1.26
	LHC	Low	White	90.24	0.86

[a]For abbreviations see Tables 1 and 2.

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Development and Testing of New Volatile Corrosion Inhibitors for Multimetal Systems

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Four new organic volatile corrosion inhibitors (VCIs) were synthesized using 1-(2-aminoethyl)-2-dec-9-enyl-2-imidazoline salicylic acid, nitrobenzoic acid, phthalic acid, and cinnamic acid. They were evaluated as corrosion inhibitors of aluminum, mild steel, brass, and copper. The weight loss, Eschke test, sodium chloride (NaCl) inoculation test, and sulfur dioxide (SO_2) test methods were used. All of the investigated VCIs exhibited good inhibition efficiency for each metal. Cinnamate salt showed the best result.

Corrosion may be defined as the destruction or deterioration of a metal caused by reactions with its environment.[1] Corrosion commonly occurs at metal surfaces in the presence of oxygen and moisture, and it involves two electrochemical reactions. Oxidation takes place at the anodic site and reduction occurs at the cathodic site. In acidic media hydrogen evolution reaction predominates. In a neutral medium, however, reduction of oxygen takes place.

Corrosion inhibitors reduce or prevent these reactions. Inhibitors adsorb onto the metal surface and act by forming a barrier to oxygen and moisture, complexing with metal ions, or removing corrodants from the environment. Some inhibitors facilitate formation of passivating film on the metal surface.

Volatile corrosion inhibitors (VCIs) are used to protect metallic articles and equipment in an enclosed atmosphere.[2] The choice of a chemical compound as a vapor phase corrosion inhibitor depends on its vapor pressure and efficiency to prevent corrosion by forming a protective film.

Numerous corrosion inhibition studies have utilized aliphatic amines, alicyclic amines, and their salts as VCIs for various industrial metals and alloys.[3-5] Fatty acid amines have been shown to be more effective than cyclic amines and aromatic amines.[5] Rajagopalan, et al.,[6] examined 1, 3-dinitrobenzene [$C_6H_4(NO_2)_2$] with β-naphthol ($C_{10}H_7OH$) as a VCI in a sulfur dioxide (SO_2) and chloride atmosphere. Subramanian, et al.,[7] studied the corrosion-inhibitive performance of cyclohexylamine (CHA) ($C_6H_{11}NH_2$) salts and dicyclohexylamine (DCHA) [$(C_6H_{11})_2NH$] salts on copper, mild steel, and zinc in an SO_2 environment. DCHA exhibited 70.86, 85.15, and 91.81% inhibition efficiency (IE) levels on mild steel, copper, and zinc, respectively. Subramanian, et al.,[8] recently studied the corrosion-inhibition behavior of morpholine (C_4H_8ONH) and its three salts—morpholine carbonate, borate, and phosphate salts. Of these, morpholine and its carbonate salt exhibited 90 and 85% IE, respectively, while the other salts gave <40% IE.

Continuing their recent work on VPIs,[9,10] the authors tested the inhibiting properties of four organic VPIs: 1-(2-aminoethyl)-2dec-9-enyl-2-imizazoline salicylate (ADIS), 1-(2-aminoethyl)-2-dec-9-enyl-2-imizazoline nitrobenzoate

TABLE 1

VCI CORROSION TESTING PROCEDURES

Test Method	Arrangement	Accelerating Agent	Test Conditions
Conical flask method[11]	Metal specimen suspended in 250-mL conical flask containing 500 ppm of inhibitor	25 mL of water + glycerin mixture to create 90% RH	40°C, 90% RH for 12 h and at room temperature for another 12 h; test duration = 20 days
Eschke test[12]	Metal specimen wrapped in single layer of inhibitor (1.1 mg/cm^2) impregnated Kraft paper	25 mL of water + glycerin mixture to create 90% RH	40°C, 90% RH for 12 h and at room temperature for another 12 h; test duration = 14 days
SO_2 test[12]	Metal specimens were placed inside 1-L glass containers containing weighed VCI	0.4 g of sodium thiosulfate ($Na_2S_2O_3 \cdot 5H_2O$) was placed inside the container containing 1 N sulfuric acid (H_2SO_4). 50-mL-capacity beaker containing 30 mL aqueous solution of salt (1% ammonium chloride [NH_4Cl] + 1% $NaSO_4$) was also placed inside the container	50°C, 90% RH for 16 h and room temperature for another 8 h; Test duration = 24 h
Salt-inoculation test[12]	Metal specimen with 10 to 12 particles of NaCl deposited at random to one side of metal surface wrapped with inhibitor (1.1 mg/cm^2) impregnated Kraft paper	25 mL of water + glycerin mixture to create 90% RH	40°C, 90% RH for 12 h and at room temperature for another 12 h; test duration = 14 days

(ADIN), 1-(2-aminoethyl)-2-dec-9-enyl-2-imizazoline phthalate (ADIP), and 1-(2-arninoethyl)-2-dec-9-enyl-2-imizazoline cinnamate (ADIC) on aluminum, mild steel, brass, and copper.

Experimental Procedures

MATERIALS

Aluminum, mild steel, brass, and copper were used in the tests.

Sizes were 2.5 by 2.0 by 0.025 cm for the conical flask method and 5.0 by 2.0 by 0.025 cm for the Eschke test, SO_2 test, and salt-inoculation test.

CORROSION TESTING

The VCIs were tested using the procedures shown in Table 1.

Synthesis of the Organic Compounds

1-(2-aminoethyl)-2-dec-9-enyl-2-imizazoline was synthesized according to the procedure reported by Pattison.[13] The salts were prepared by dissolving the equimolar fatty acid imidazoline and organic acids in ethanol (C_2H_5OH). The reaction mixture was stirred for 1 h at 40°C. The precipitated compounds—M.P°C (ADIS = 62, ADIN = 210, ADIP = 140, ADIC = 88)—were filtered and crystallized from ethanol. All compounds were purified by crystallization, and their purity was confirmed by thin-layer chromatography.

TABLE 2

WEIGHT-LOSS PARAMETERS OBTAINED FOR 500-PPM CONCENTRATION OF VCI AT 40 ± 1 K AND 90% RH FOR 20 DAYS FOR VARIOUS METALS

System	Weight Loss (mg)	IE (%)	Corrosion Rate (mmpy × 10^{-2})
Aluminum	60.6	—	40.9
ADIS	11.4	81.19	7.69
ADIN	11.3	81.36	7.62
ADIP	11.0	81.85	7.42
ADIC	10.6	82.51	7.15
Mild steel	34.5	—	8.00
ADIS	1.8	94.87	0.42
ADIN	1.5	95.75	0.35
ADIP	1.3	96.25	0.30
ADIC	1.2	96.62	0.28
Brass	8.4	—	1.79
ADIS	2.2	73.18	0.47
ADIN	1.8	78.77	0.38
ADIP	1.2	86.03	0.25
ADIC	1.0	88.26	0.21
Copper	5.7	—	1.16
ADIS	2.4	58.62	0.49
ADIN	1.8	68.96	0.36
ADIP	1.5	74.13	0.30
ADIC	1.2	79.31	0.24

Vapor Pressure Determination

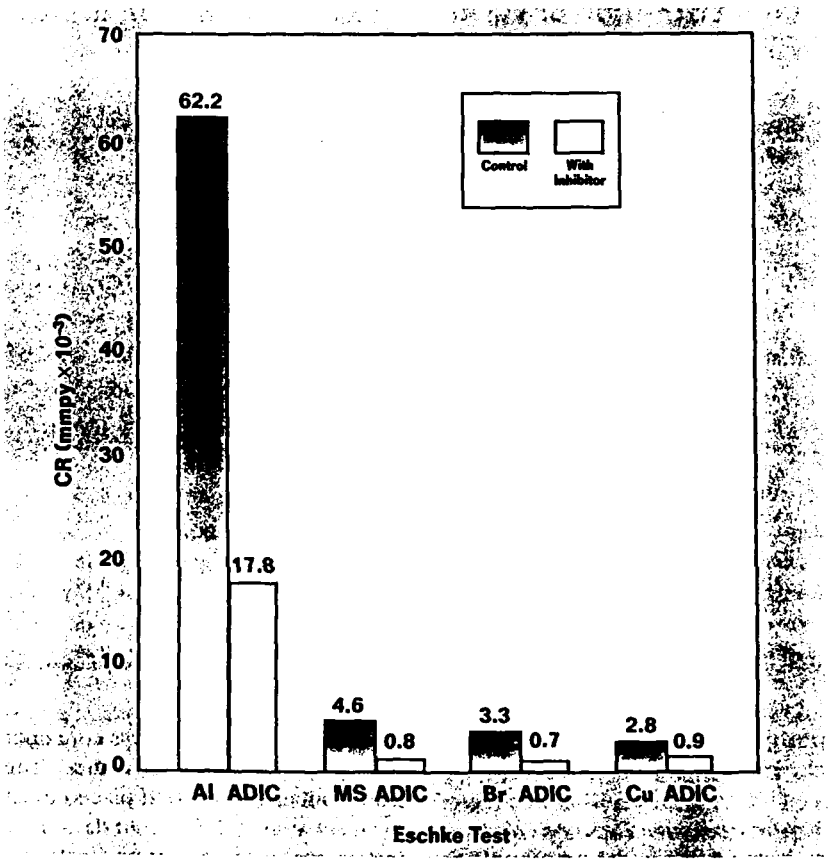
A standard Knudsen method[14] was used to determine the vapor pressure of the inhibitors. The weighed compound was placed in a glass container having a 1-mm-diameter orifice. The glass container was then placed in an oven set at 40 ± 1°C for 20 days. Loss in mass was measured by an electronic balance, and the values were put into Equation (1):

TABLE 1

VISUAL OBSERVATIONS OF THE METAL SURFACE IN THE PRESENCE AND ABSENCE OF ADIC FROM VARIOUS METHODS

System	Eschke Test	SO_2 Test	Salt-Inoculation Test
Aluminum (control)	Heavy dulling, grayish-white surface	Slight dulling	Moderate corrosion around all nuclei; heavy dulling
ADIC	Slight dulling	No effect; bright surface	Corrosion confined to nuclei; slight dulling
Mild steel (control)	Moderate to heavy rusting	Severely rusted all over the surface	Entire surface covered with patches of brownish-red spots
ADIC	One to two rusted spots	No rusting; bright surface	Corrosion restricted to nuclei; rest of the surface bright and unattacked
Brass (control)	Moderate-to-heavy tarnishing	Moderate-to-heavy tarnishing	Corrosion around nuclei
ADIC	Slight tarnishing	Slight tarnishing	Slight corrosion around nuclei
Copper (control)	Moderate-to-heavy tarnishing	Heavy tarnishing	Corrosion around nuclei
ADIC	Slight tarnishing	Slight tarnishing	Slight corrosion around nuclei

FIGURE 1



Results of Eschke test. CR for aluminum, mild steel, brass, and copper in the absence and presence of ADIC at 40 ± 1°C and 90% relative humidity (RH) for 14-day test duration.

$$p = \frac{W}{At} \times \left(\frac{2\pi RT}{M}\right)^{1/2} \quad (1)$$

where p = vapor pressure of the inhibitor in mm Hg, A = area of the orifice in m^2, t = time of exposure in seconds, W = weight of evaporated substance in kg, T = temperature in K, M = molecular mass of the compound in kg, and R = gas constant (8.314 J K^{-1} mol^{-1}). The following vapor pressures in mm Hg were determined:

- ADIS—91.0×10^{-7}
- ADIN—69.0×10^{-7}
- ADIP—15.8×10^{-7}
- ADIC—13.6×10^{-6}

Results and Discussion

CONICAL FLASK METHOD

Table 2 summarizes the values of percentage inhibition efficiency (%IE) and corrosion rate (CR) obtained by weight loss methods at 500 ppm concentration of VCIs for different metals at 40 ± 1°C. The %IE was calculated using Equation (2):

$$\%IE = [(CR^\circ - CR)/CR^\circ] \times 100 \quad (2)$$

where CR° and CR are the corrosion rates in the absence and presence of inhibitors, respectively. The corrosion rate was calculated using Equation (3):

$$CR = \frac{K \times W}{A \times T \times D} \qquad (3)$$

where K is a constant (8.76×10^4 for mmpy), W is weight loss in gm, A is the area of the coupon in cm^2, T is time of exposure in hours, and D is density of the metal in gm/cm^3.

All VCIs have shown good IE, which may be attributed to the formation of a physical barrier between the metal and corrosive environment by the interaction of metal and inhibitor molecules. The corrosion-inhibiting action of the VCIs stems from the presence of a lone pair of electrons present on the N atoms of the inhibitor molecules. The electrons facilitate adsorption of these inhibitors onto the metal surface. In the present investigation, cinnamate salt (ADIC) exhibited the highest IE for all of the metals. It gave 82.5, 96.6, 88.3, and 79.3% for aluminum, mild steel, brass, and copper, respectively. High IE of ADIC may be attributed to the presence of an additional π-bond between C = C that further facilitates greater adsorption of ADIC on the metal surface.

ESCHKE TEST

Table 3 represents the summary of the visual observations of the test. A large spread of results was obtained. Figure 1 graphically represents all of the metals with respect to CR in the absence (control) and presence of ADIC.

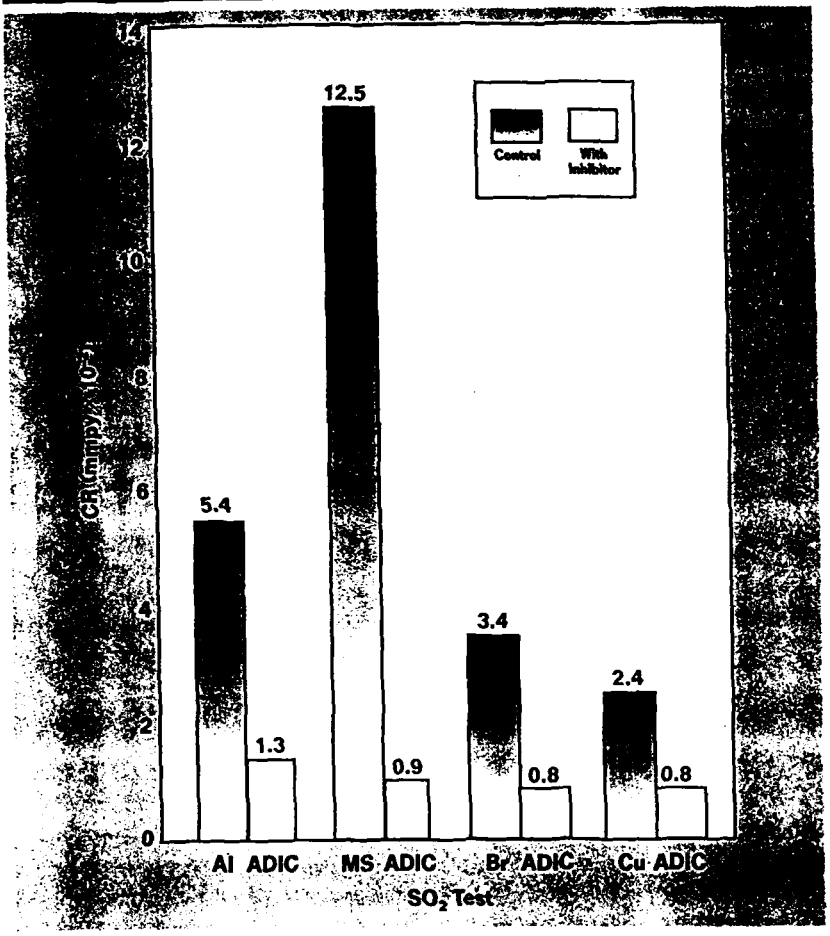
SO_2 TEST

Figure 2 shows the result obtained in the presence of SO_2. The CR values were reduced considerably in the inhibited metal specimens. Table 3 presents a summary of the visual observations of the test. Corrosion of all the metals was reduced considerably in the presence of ADIC.

Salt-Inoculation Test

Figure 3 illustrates the result obtained when the metals are inoculated with sodium chloride (NaCl) in the absence (control) and presence of ADIC. Table 3 summarizes the visual observations of the test. The authors also visually observed that, in the case of inhibited samples, the extent of corrosion around the salt nuclei was restricted and further spreading of the corrosion was arrested to a considerable extent.

FIGURE 2



CR of different metals in the absence and presence of ADIC in SO_2 environment for 24-h test duration.

MECHANISM OF CORROSION INHIBITION

Inhibition of metallic corrosion in the presence of 1-(2-aminoethyl)-2-dec-9-enyl-2-imizazoline salts involves vaporization of the inhibitors in a non-dissociated molecular form, followed by hydrolysis of the salts into carboxylate anions ($RCOO^-$) and organic cations ($RCONHNH_3^+$). Anions are adsorbed on the anodic site of the metal and inhibit anodic reaction while organic cations are adsorbed on the cathodic side, thereby preventing cathodic reaction.[15]

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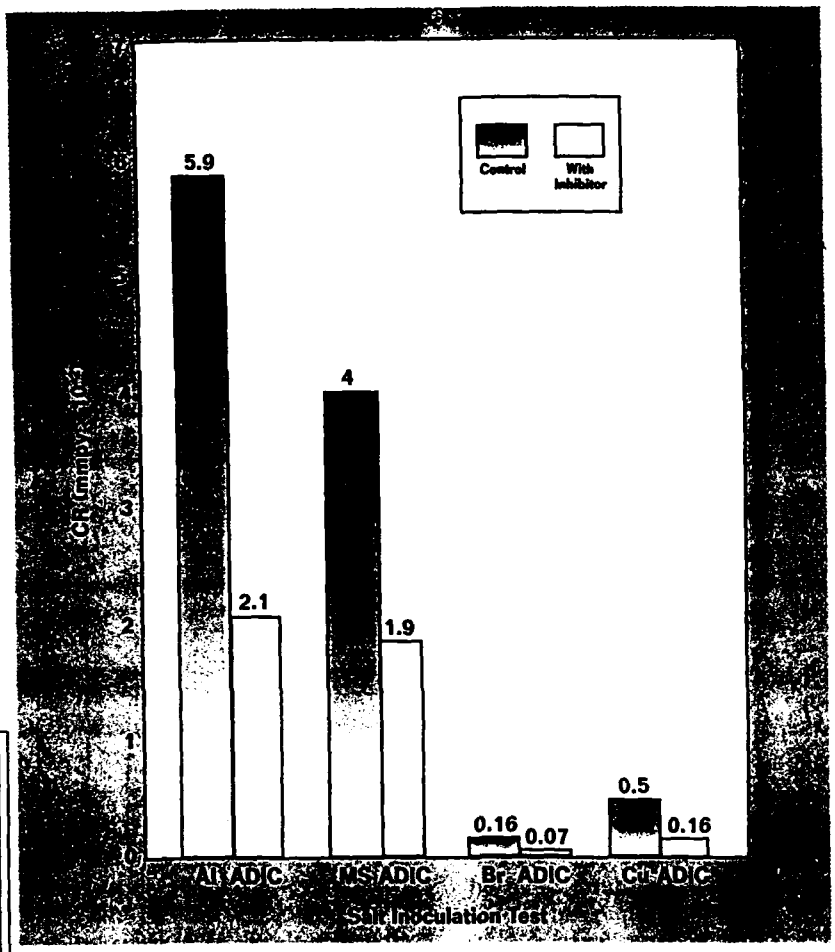
FIGURE 3



CR of different metals in the absence and presence of ADIC in the presence of salt at 40 ± 1°C and 90% RH for 14-day test duration.

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INHIBITION OF METALLIC CORROSION BY SOME 1-(2-AMINOETHYL)-2-UNDECYL-2-IMIDAZOLINE SALTS UNDER VAPOUR PHASE CONDITIONS

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Four organic volatile corrosion inhibitors (VCIs) were synthesized using 1-(2-aminoethyl)-2-undecyl-2-imidazoline with various acids such as maleic acid, nitrobenzoic acid, phthalic acid and cinnamic acid and evaluated as corrosion inhibitors of aluminium, mild steel, brass and copper by weight loss method. Eschke test method, sodium chloride inoculation test method and sulfur dioxide (SO_2) test method were also carried out to investigate the corrosion inhibiting effect of the compounds. All the investigated VCIs exhibited good inhibition efficiency (IE) for all the metals. Cinnamate salt showed best result among all studied compounds for all the metals.

Keywords: Esche test, ferrous and non-ferrous metals, 2- imidazoline, salt inoculation test, sulfur dioxide test, volatile corrosion inhibitor.

INTRODUCTION

The destructive attack of a metal by chemical and electrochemical reaction environment is known as corrosion [1]. Corrosion causes enormous economic losses. In USA, the economic losses have been estimated as high $270 b per year. The use of inhibitors is one of the most cost effective methods of protecting corrosion.

The volatile corrosion inhibitors are used to protect metallic articles and equipments in enclosed atmosphere [2]. The choice of a chemical compound as a vapour phase corrosion inhibitor (VCI) depends on its vapour pressure and efficiency to prevent corrosion by forming a protective film. There are numerous investigations on corrosion inhibition studies utilizing aliphatic amines, alicyclic amines and their salts as VCIs for various industrial metals and alloys [3-5]. Fatty acid amines are more effective than cyclic amines and aromatic amines [5]. 1,3-dinotrobenzene with β-naphthol was examined as VCI in SO_2 and chloride atmosphere by Rajagopalan et al. [6]. Subramanian et al. [7] studied corrosion inhibitive performance of cycloheyxlamine (CHA) salts and dicyclohexylamne (DCHA) salts on copper, mild steel and zinc in SO_2 environment. DCHA exhibited 70.86, 85.15 and 91.81% inhibition efficiency (IE) in mild steel, copper and zinc respectively. Subramanian et al. [8] has recently studied the corrosion inhibition behaviour of morpholine and its three salts such as morpholine carbonate, borate and phosphate salts. Of these, morpholine and its carbonate salt exhibited 90% and 85% IE, respectively, while the other salts are less than 40% IE.

Continuing our recent work [9-10] on vapour phase corrosion inhibitors, we report here the inhibiting properties of four organic vapour phase inhibitors (VCIs) namely, 1-(2-aminoethyl)-2-undecyl-2-imidazoline maleate (AUIM), 1-(2-amino

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ethyl)-2-undecyl-2-imidazoline nitrobenzoate (AUIN), 1-(2-aminoethyl)-2- undecyl-2-imidazoline phthalate (AUIP) and 1-(2-aminoethyl)-2- undecyl- 2-imidazoline cinnamate (AUIC) on aluminium, mild steel, brass and copper.

EXPERIMENTAL

Synthesis of the organic compounds

1-(2-aminoethyl)-2-undecyl-2-imidazoline was synthesized according to the procedure reported in the literature [11] and the salts were prepared by dissolving equimolar fatty acid imidazoline and organic acids in ethanol. The reaction mixture was stirred for 1 hour at 313 K. The precipitated compounds were filtered and crystallized from ethanol. MP^0C (AUIM = 115, AUIN = 95, AUIP = 90, AUIC = 62). Name and molecular structure of the compounds are presented in Scheme 1.

Weight loss measurements

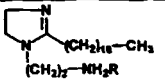
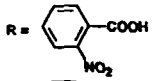
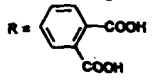
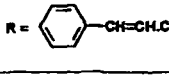
Corrosion experiments were carried out according to the procedure reported in the literature [12] using various ferrous and non- ferrous metals viz. aluminium, mild steel, brass and copper. The specimens of size 2.5 cm by 2.0 cm by 0.025 cm were used for weight loss measurement studies. Weight loss experiments were carried out in the presence and absence of inhibitors at a fixed concentration of 500 ppm, using tight fitting rubber cork 250 ml conical flasks containing 25 ml of water-glycein mixture to produce 90% relative humidity. The concentration of the inhibitors used for the study was taken according to the volume of the conical flask. The metal specimens were suspended in these bottles by nylon gas and just below these specimens weighed VCIs samples were kept in a glass container as not to be in contact with the liquid kept inside the conical flask. A battery of conical flasks were kept in an air thermostat set at temperature 313 ± 1 K and 90% relative humidity during the day and were removed at night to allow condensation of moisture on metal specimen. The experiment was conducted for 20 days. The coupons were placed in inhibited acid bath to remove corrosion products then weighed.

Eschke test

Eschke test was carried out as per procedure reported in the literature [13] using various metals. Polished strips of size 5.0 cm by 2.0 cm by 0.025 cm were wrapped in single layer of inhibitor impregnated Kraft papers and suspended in climatic cabinet maintained at 90% relative humidity. 1 $gm.ft^{-2}$ of various inhibitors were used for the experiment. The temperature cycles was set at 313 ± 1 K for 12 hours and at room temperature of another 12 hours for condensation of the moisture. The duration of the test was 14 days. A similar experiment was done with metals covered with untreated Kraft paper (control).

Sulfur dioxide (SO_2) test [13]

Clean and dry metal specimens 5 cm by 2 cm by 0.25 cm were placed inside one litre glass container. Weighed VCI compound was kept inside the container. A small beaker containing 0.04 gm of sodium thiosulphate was placed inside the container. 50 ml capacity baker containing 30 ml aqueous solution of salt (1% NH_4Cl + 1% $NaSO_4$) was placed inside the container. 0.5 ml of 1 N sulfuric acid was directly added to the beaker containing sodium thiosulphate and the glass container was immediately sealed. The glass container was placed in an oven set at 313 ± 1 K for the duration of 16 hours and at 283 K for

S. No.	Formula	Designation and Abbreviation
		
1.	R = $HO_2CCH=CHCO_2H$	1-(2-aminoethyl)-2-undecyl-2-imidazoline maleate (AUIM)
2.	R = 	1-(2-aminoethyl)-2-undecyl-2-imidazoline nitrobenzoate (AUIN)
3.	R = 	1-(2-aminoethyl)-2-undecyl-2-imidazoline phthalate (AUIP)
4.	R = 	1-(2-aminoethyl)-2-undecyl-2-imidazoline cinnamate (AUIC)

Scheme 1: Name and molecular structure of the compounds used

another 8 hours. A similar experiment was done with the one litre glass container in absence of VCI compound (control).

Salt inoculation test [6]

0.1 g of sodium chloride was placed in 200 ml carbon tetrachloride and the whole solution was stirred by a magnetic stirrer. The metal specimen 5 cm by 2 cm by 0.25 cm was introduced in the stirred solution for 3-4 seconds and taken out when approximately 10-12 particles of salt were deposited at random on each side of metal surface One side of the metal surface was cleaned off the salt particles and the whole metal surface was wrapped in single layer of inhibitor impregnated Kraft papers and suspended in climatic cabinet maintained at 90% relative humidity. 1 $gm.ft^{-2}$ of various inhibitors were sued for the experiment. The temperature cycle was set at 313 ± 1 K for 12 hours and at room temperature for another 12 hours for condensation of the moisture. The duration of the test was 14 days. A similar experiment was done with metals covered with untreated Kraft paper (control).

Vapour pressure determination

A standard Knudsen method [14] was used to determine the vapour pressure of the inhibitors. Weighed compound was placed in a glass container having an orifice of 1 mm diameter. The glass container was then placed in an oven set at 313 ± 1 K for 20 days. Loss in mass was measured by an electronic balance and the values were put into the formula given below.

TABLE I: Vapor pressure [a] of VCIs

Vapor pressure (mmHg[b])	Compounds
14.5×10^{-6}	AUIM
5.6×10^{-6}	AUIN
7.4×10^{-6}	AUIP
6.9×10^{-6}	AUIC

a = as determined from Knudsen method
b = millimeter of mercury

$$p = \frac{W}{At} \times \left(\frac{2\pi RT}{M}\right)^{1/2} \quad (1)$$

where p is vapour pressure of the inhibitor in Pascal (Pa), A is area of the orifice in m^2, t is time of exposure in second, W is weight of evaporated substance in kilogram, T is temperature in Kelvin, M is molecular mass of the compound in kilogram and R is gas constant (8.314 $JK^{-1}.mol^{-1}$). Values of the vapour pressure obtained are given in Table I.

TABLE II: Weight loss parameters[a] obtained for 500 ppm concentration of VCIs at 313 ± 1 K and 90% relative humidity for 20 days for various metals

System	Weight loss (g)	IE[b] (%)	Corrosion rate (mmpy[c] x 10^{-2})
Aluminium	60.6	—	40.90
AUIM	15.8	74.91	10.26
AUIN	12.7	79.04	8.57
AUIP	12.4	79.53	8.37
AUIC	11.7	80.70	7.89
Mild Steel	34.5	—	8.00
AUIM	3.4	90.12	0.79
AUIN	2.0	94.25	0.46
AUIP	1.9	94.50	0.44
AUIC	1.1	96.87	0.25
Brass	8.4	—	1.83
AUIM	1.5	82.51	0.32
AUIN	1.3	85.24	0.27
AUIP	0.8	90.71	0.17
AUIC	0.6	93.44	0.12
Copper	5.7	—	1.16
AUIM	1.0	82.75	0.20
AUIN	0.8	86.20	0.16
AUIP	0.6	89.65	0.12
AUIC	0.5	91.37	0.10

a = as determined from weight loss measurements
b = IE, inhibition efficiency; c = mmpy, millimeter per year

TABLE III: Visual observations of the metal surface in the presence and absence of AUIC from various methods

System	Visual observations		
	Eschke test	SO_2 test	Salt inoculation test
Aluminium (control)	Heavy dulling, grayish white surface	Slight dulling	Moderate rusting around all nuclei; heavy dulling
AUIC	Slight dulling	No effect; bright surface	Rusting confined to nuclei; slight dulling
Mild steel (control)	Moderate to heavy rusting	Severely rusted all over the surface	Whole surface covered with patches of brownish-red spots
AUIC	1-2 rusted spot	No rusting; Bright surface	Rusting restricted to nuclei, rest of the surface bright & unattacked
Brass (control)	Moderate to heavy tarnishing	Moderate to heavy tarnishing	Rusting around nuclei
AUIC	Slight tarnishing	Slight tarnishing	Slight rusting around nuclei
Copper (control)	Moderate to heavy tarnishing	Heavy tarnishing	Rusting around nuclei
AUIC	Slight tarnishing	Slight tarnishing	Slight rusting around nuclei

RESULTS AND DISCUSSION

Weight loss measurement

The values of percentage inhibition efficiency (%IE) and corrosion rate (CR) obtained by weight loss methods at 500 ppm concentration of VCIs for different metals are summarized in Table II. The %IE was calculated using the following equation

$$\%IE = [(CR^0 - CR)/ CR^0] \times 100 \quad (2)$$

where CR^0 and CR are the corrosion rates in the absence and presence of inhibitors, respectively. The corrosion rate was calculated using the following formula.

$$CR = \frac{K \times W}{A \times T \times D} \quad (3)$$

where K is a constant (8.76×10^4 for mmpy, millimeters per day), W is weight loss in gm, A is area of the coupon in cm^2, T is time of exposure in hour and D is density of metal in $gm.cm^{-3}$.

All VCI s have shown good IE, which may be attributed to the formation of a physical barrier between metal and corrosive environment by the interaction of metal and inhibitor molecules. The corrosion inhibiting action of the volatile corrosion inhibitors is attributed to the presence of lone pair of electrons present on the N atoms of the inhibitor molecules, which facilitate adsorption for these inhibitors onto the metal surface. In the present investigation, cinnamate salt exhibited highest IE for all the metals. It gave 80.7%, 96.8%, 93.2% and 91.3% for aluminium, mild steel, brass and copper respectively. High IE of cinnamate salt may be attributed to the presence of an additional π-bond between C = C which further facilitate greater adsorption of cinnamate salt on the metal surface.

Eschke test

The summary of the visual observations of the test is given in Table III. It is seen that a large spread of results were obtained. The graphical representation of all the metals with respect to CR in the absence (control) and presence of AUCI is shown in Fig. 1.

SO_2 test

The results obtained in the presence of sulfur dioxide is shown in Fig. 2. It is seen that values of CR was reduced considerably in the inhibited metal specimens. The summary of the visual

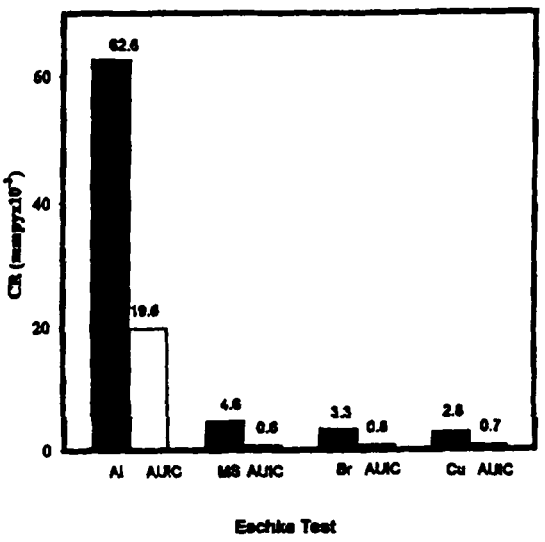


Fig. 1: Results of Eschke test
CR for aluminium, mild steel, brass and copper in absence and presence of for AUIC at 313 ± 1 K and 90% relative humidity for 14 days test duration

observations of the test is given in Table III. Corrosion of all the metals was reduced considerably in the presence of AUIC.

Salt inoculation test

The result obtained when the metals are inoculated with sodium chloride in absence

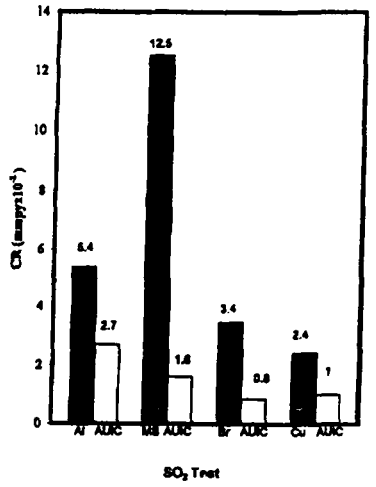


Fig. 2: Cr of different metals in absence and presence of AUIC in SO_2 environment for 24 hours of test duration

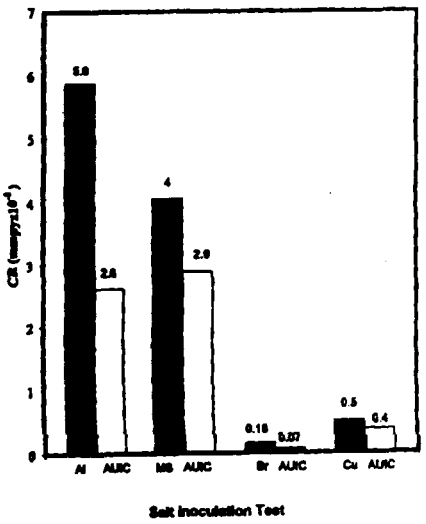


Fig. 3: CR of different metals in absecne and presence of AUIC in presence of salt at 313 ± 1 K and 90% relative humidity for 14 days test duration

(control) and presence of AUIC is shown in Fig. 3. The summary of the visual observations of the test is given in Table III. It is also observed visually that in the case of inhibited samples the extent of corrosion around the salt nuclei is restricted and further spreading of the rust was arrested to a considerable extent.

Mechanism of corrosion inhibition

Inhibition of metallic corrosion in presence of 1-(2-aminoethyl)- 2-undecyl-2-imidazoline salts involved vapourization of the inhibitors in a non-dissociated molecular form, followed by hydrolysis of the salts into carboxylate anions ($RCOO^-$) and organic cations ($RCONHNH_3^+$). Anions are adsorbed on the anodic side of the metal and inhibit anodic reaction while organic cations are adsorbed on cathodic side thereby preventing cathodic reaction [15].

CONCLUSION

- All the organic vapour phase corrosion inhibitors showed good inhibition efficiency for aluminium, mild steel, brass and copper.

- All the vapour phase corrosion inhibitors inhibited corrosion of metals by being adsorbed onto the metals surface.

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The Society for Advancement of Electrochemical Science and Technology is immensely pleased in honouring Shri.Vikas Bharadwai ...of..... Corrosion Research Laboratory, Dept. of Applied Chemistry, Faculty of Engineering and Technology, Aligarh Muslim University, Aligarh 202 002..... by presenting him/her the

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for the year 2003 in appreciation of his / her paper "Inhibition of Metallic corrosion by some 1-(2-Aminoethyl)-2-Undecyl-2-Imidazoline Salts Under Vapour Phase Conditions" which appeared in Bulletin of Electrochemistry, 19, 7 (2003) 295 and was selected as the best publication in the field of "Corrosion and its prevention".

Date: 22nd, July 2005

M Jayachandran
Secretary

Ramachandra N Galla
President

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Protection of metals by new vapour phase corrosion inhibitors

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Abstract

A few volatile corrosion inhibitors (VCIs) were synthesized using benzoic hydrazide with various aromatic aldehydes such as benzaldehyde, salicylaldehyde, cinnamaldehyde and dimethyl aminobenzaldehyde. They were evaluated as corrosion inhibitors for mild steel, brass and copper by the weight loss method. Eschke test method, sodium chloride inoculation test method and sulfur dioxide (SO_2) test method were also carried out to investigate the corrosion inhibition behavior of the compounds. The VCIs exhibited good inhibition efficiency. Benzaldehyde derivatives showed the best result.

Keywords: Volatile corrosion inhibitor; Benzoic hydrazide derivatives; Eschke test; Sodium chloride inoculation test; Sulfur dioxide test

Introduction

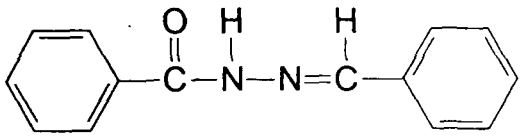
The use of volatile corrosion inhibitors (VCI) is an effective method to prevent atmospheric corrosion [1–3]. VCIs are used to protect metallic articles and equipment in closed atmosphere. The protection of the metal is due to the inhibitors volatilizing into the atmosphere surrounding the metal parts and modifying the atmosphere [4]. VCIs function by forming a bond on the metal surface and by forming a barrier layer to aggressive ions. The vapour pressure (VP) of the compounds used as VCIs must possess some optimum values (~ 10^{-2} – 10^{-7} mm Hg) [5].

Continuing our recent work [6–9] on vapour phase corrosion inhibitors, we report here the inhibiting properties of four organic vapour phase inhibitors, namely, bezalidene benzoic hydrazide (BBH), salicylidene benzoic hydrazide (SBH), cinnamalidene benzoic hydrazide (CBH) and dimethyl aminobezalidene benzoic hydrazide (DBH) for the corrosion of mild steel, brass and copper.

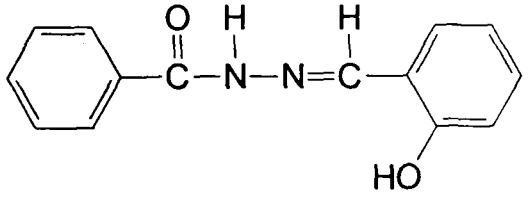
Experimental

Synthesis of inhibitors

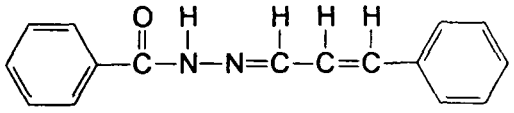
Benzoic hydrazide was synthesized according to the procedure reported in the literature [10], and their Schiff's bases were prepared by dissolving equimolar amounts of benzoic hydrazide and aromatic aldehydes in ethanol. The reaction mixture was refluxed for 1 h. The precipitated compounds were filtered and crystallized from ethanol. All compounds were purified by crystallization and their purity was confirmed by thin layer chromatography. The names, structural formulae and melting points of the compounds are given in Fig. 1.



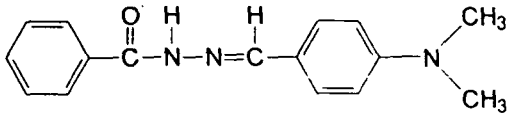
Benzalidene benzoic hydrazide (BBH)
[441 K]



Salicylidene benzoic hydrazide (SBH)
[421 K]



Cinamalidene benzoic hydrazide (CBH)
[412 K]



Dimethylamonobezalidene benzoic hydrazide (DBH)
[401 K]

Fig. 1. Names, structural formulae and melting points of the compounds used.

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Conical flask method

Corrosion experiments were carried out according to the procedure reported in the literature [11] using mild steel, brass and copper. The specimens of size 2.5 cm x 2.0 cm x 0.025 cm were used for weight loss measurements. Weight loss experiments were carried out with and without inhibitors at a fixed concentration of 500 ppm. Conical flasks of 250 ml capacity containing 25 ml of water-glycerin mixture fitted with rubber corks to produce 90% relative humidity were used. The concentration of the inhibitors used for the study was taken according to the volume of the conical flask. The metal specimens were suspended in these bottles by nylon tags and just below these specimens weighed VCIs samples were kept in a glass container so as not to be in contact with the liquid kept inside the conical flask. A battery of conical flasks were kept in an air thermostat set at a temperature of 313 ± 1 K and 90% relative humidity during the day and were removed at night to allow condensation of moisture on the metal specimens. The experiment was conducted for 20 days. The coupons were placed in inhibited acid baths to remove corrosion products and then weighed. The experiment was run in duplicate and the average values of weight loss were taken for the study.

Eschke test

Eschke test was carried out as per procedure reported in the literature [12]. Polished strips of size 5.0 cm x 2.0 cm x 0.025 cm were wrapped in a single layer of inhibitor–impregnated Kraft paper and suspended in a climatic cabinet maintained at 90% relative humidity. A 1 g.ft.$^{-2}$ of various inhibitors were used for the experiment. The temperature cycle was set at 313 ± 1 K for 12 h and at 283 K for another 12 h for condensation of the moisture. The duration of the test was 20 days. A similar experiment was done with metals covered with untreated Kraft paper (control).

Sulfur dioxide test [12]

Clean and dry metal specimens of size 5.0 cm x 2.0 cm x 0.025 cm were placed inside a one-liter glass container. A weighed amount of the VCI compound was kept inside the container. A small beaker containing 0.04 g of sodium thiosulphate was placed inside the container. A 50 ml beaker containing 30 ml of the aqueous solution of 1% NH_4Cl + 1% Na_2SO_4 was placed inside the container. 0.5 ml of 1N sulfuric acid was directly added to the beaker containing sodium thiosulphate and the glass container was immediately sealed. The glass container was placed in an oven set at 313 K ± 1 K for 16 h and at 283 K for another 8 h. A similar experiment was done with the one-liter glass container without addition of the VCI compound (control).

Salt inoculation test [5]

0.1 g of sodium chloride was placed in 200 ml carbon tetrachloride and the whole solution was stirred on a magnetic stirrer. Metal specimens of size 5.0 cm x 2.0 cm x 0.025 cm were introduced in the stirred solution for 3–4 s and taken out when approximately 10–12 particles of salt were deposited at random on each side of the metal surface. One side of the metal surface was cleaned off the salt particles and the whole metal surface was wrapped in a single layer of inhibitor–impregnated Kraft paper and suspended in a climatic cabinet maintained at 90% relative humidity. An amount of 1 g.ft.$^{-2}$ of various inhibitors was used for the experiment. The temperature cycle was set at 313 ± 1 K for 12 h and at room temperature for another 12 h for condensation of the moisture. The duration of the test was 20 days. A similar experiment was done with metals covered with untreated Kraft paper (control).

Vapour pressure determination

A standard Knudsen method [13] was used to determine the vapour pressure of the inhibitors. The weighed compound was placed in a glass container having an orfice of 1.0 mm diameter. The glass container was then placed in an oven set at 313 ± 1 K for 20 days. Loss in mass was measured on an electronic balance. The vapour pressure, p, of the inhibitor in mm Hg, was calculated using

$$p = \frac{W}{At} \times \left(\frac{2\pi RT^{1/2}}{M} \right)$$

where A = area of the orfice in m^2, t = time of exposure in second, W = weight of evaporated substance in kilogram, T = temperature in Kelvin , M = molecular mass of the compound in kilogram, and R = gas constant (8.314 J.K^{-1}mol^{-1}). Values of the vapour pressure obtained are given in Table I.

Table I
Vapour pressures of VCIs.

Compound	Vapour Presssure (mm Hg)
Benzalidene benzoic hydrazide (BBH)	5.98 x 10^{-7}
Salicylidene benzoic hydrazide (SBH)	8.68 x 10^{-7}
Cinamalidene benzoic hydrazide (CBH)	0.85 x 10^{-7}
Dimethylamonobezalidene benzoic hydrazide (DBH)	25.52 x 10^{-7}

Results and Discussion

Conical flask method

The values of the percentage inhibition efficiency (*%IE*) and corrosion rate (*CR*) obtained by the weight loss method with and without the VCIs for the different metals at 313 ± 1 K are summarized in Table II. The *%IE* was calculated using the following equation:

$$\%IE = [(CR^0 - CR) / CR^0] \times 100$$

Table II
Weight loss parameters obtained with 500 ppm concentration of VCIs at 313 K ± 1 K and 90% relative humidity for 20 days for various metals

System	Mild steel			Brass			Copper		
	WL (mg)	*IE* (%)	*CR* (mpy x 10^{-2})	*WL* (mg)	*IE* (%)	*CR* (mpy x 10^{-2})	*WL* (mg)	*IE* (%)	*CR* (mpy x 10^{-2})
Conical flask method									
Control	34.5	–	320	8.4	–	71.0	5.7	–	46.0
BBH	1.0	97.12	9.2	0.3	96.46	2.5	0.3	94.75	2.4
SBH	1.2	96.62	10.8	0.5	94.04	4.2	0.4	93.02	3.24
CBH	1.8	94.87	16.4	0.9	89.26	7.6	0.5	91.22	4.08
DBH	2.0	94.25	18.4	1.2	85.95	10.0	0.6	89.50	4.88
Eschke test									
Control	4.8	–	22.00	3.1	–	13.10	2.2	–	8.96
BBH	0.6	87.36	2.78	0.8	74.88	3.39	0.8	63.61	3.26
SBH	1.0	78.90	5.04	1.0	67.63	4.24	1.0	54.46	4.08
CBH	1.1	76.90	5.08	1.3	57.93	5.51	1.1	50.00	4.48
DBH	1.3	72.72	6.00	1.4	54.73	5.93	1.3	40.84	5.30
Sulfur dioxide test									
Control	5.4	–	501.44	1.2	–	102.68	1.3	–	106.36
BBH	0.7	87.04	64.98	0.1	91.68	8.54	0.1	92.30	8.18
SBH	1.5	72.23	139.26	0.3	75.03	25.63	0.3	76.92	24.54
CBH	1.9	64.83	176.39	0.5	58.39	42.72	0.4	69.23	32.72
DBH	2.2	59.27	204.24	0.6	50.07	51.26	0.6	53.85	49.08
Salt inoculation									
Control	44.7	–	207.4	1.9	–	8.04	4.2	–	17.12
BBH	20.7	53.69	96.04	0.7	63.08	2.96	2.0	52.33	8.16
SBH	23.0	48.54	106.72	0.9	52.53	3.80	2.4	42.81	9.79
CBH	26.0	41.83	120.64	1.0	47.26	4.24	2.8	33.29	11.42
DBH	28.1	37.13	130.38	1.3	31.84	5.48	3.1	26.16	12.64

where CR^0 and CR are the corrosion rate in the absence and presence of the inhibitors, respectively. The corrosion rate was calculated using the formula:

$$CR = \frac{K \times W}{A \times T \times D}$$

where K is a constant (3.45 x 104 in mpy), W is weight loss in g, A is area of the coupon in cm^2, T is time of exposure in hour and D is density of metal in $g.cm^{-3}$.

All VCIs show good *IE*, which may be attributed to the formation of a physical barrier between the metal and corrosive environment by the interaction of the metal and the inhibitor molecules. Difference in their inhibiting action, however, can be explained by their molecular structure.

Eschke test

The values of *%IE* and *CR* obtained by the Eschke test are summarized in Table II. A summary of the visual

metal surface causing less adsorption and, thereby, less inhibition.

Conclusions

All the tested organic inhibitors showed good inhibition efficiency (*IE*) for mild steel, brass and copper. BBH exhibited the highest IE for all the metals. The order of the *IE* for the various inhibitors for the metals follows the order BBH > SBH > CBH > DBH.

Acknowledgement

Two of the authors (DJ) and (VB) thankfully acknowledge CSIR, New Delhi, India for the award of Research Associateship and Senior Research Fellowship, respectively.

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Prevention of metallic corrosion by some salts of benzoic hydrazide under vapour phase conditions

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Three volatile corrosion inhibitors (VCIs) namely, benzoic hydrazide benzoate (BHB), benzoic hydrazide salicylate (BHS), and benzoic hydrazide nitrobenzoate (BHN), were synthesized and evaluated as corrosion inhibitors of mild steel, brass and copper by weight loss method. Eschke test method, sodium chloride inoculation test method and sulphur dioxide (SO_2) test method were also carried out to investigate the corrosion inhibiting effect of the compounds. All the investigated VCIs exhibited good inhibition efficiency (*IE*) for all the metals. Benzoate salt showed best result among all the studied compounds for all the metals.

Keywords: Brass, copper, benzoic hydrazide, mild steel, volatile corrosion inhibitor.

IPC Code: C07C 243/00; C23F 11/10

Corrosion is defined as the destruction or deterioration of metals. Corrosion causes heavy economic losses. In India, the annual economic losses have been estimated as high as Rs.2500 crore. Corrosion commonly occurs at metal surfaces in the presence of oxygen and moisture and involves two electrochemical reactions. Oxidation takes place at anodic site and reduction occurs at cathodic site. In acidic medium hydrogen evolution reaction predominates, while in neutral medium reduction of oxygen takes place. Corrosion inhibitors reduce or prevent these reactions, they are adsorbed onto the metal surface and act by forming a barrier to oxygen and moisture, by complexing with metal ions or by removing corrodants from the environment, some of the inhibitors facilitate formation of passivating film on the metal surface.

Use of volatile corrosion inhibitor (VCI) is an effective method to prevent atmospheric corrosion[1-3]. The VCIs are used to protect metallic articles and equipments in enclosed atmosphere[4]. The protection of metal is due to the inhibitors volatizing into the atmosphere surrounding the metal parts and modifying the atmosphere[5]. VCI functions by forming a bond on the metal surface and by forming a barrier layer to aggressive ions[4]. On contact with the metal surface, the vapour of the VCI condenses and is hydrolysed by moisture to release protective ions. The choice of a chemical compound as VCI depends on its vapour pressure as well as its efficacy in preventing corrosion by forming a protective film. The vapour pressure (VP) of the compounds used as VCI must possess some optimum values. It must not have too high or too low a VP. Substitution of an organic compound with an inorganic functional group may give a desirable property.

Recent work[6-9] on vapour phase corrosion inhibitors has been extended here by exploring the inhibiting properties of three organic vapour phase inhibitors (VCIs) namely, benzoic hydrazide benzoate (BHB), benzoic hydrazide salicylate (BHS), and benzoic hydrazide nitrobenzoate (BHN), on mild steel, brass and copper.

Experimental Procedure

Inhibitors

Benzoic hydrazide was synthesized according to the reported procedure[10] and the salts were prepared by dissolving equimolar quantities of benzoic hydrazide and organic acids in ethanol. The reaction mixture was stirred for 1 h at 40 °C. The precipitated compounds were filtered and crystallized from ethanol. All compounds were purified by crystal-

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lization and their purity was confirmed by thin layer chromatography. Name and structural formulas of the compounds are given in Table 1.

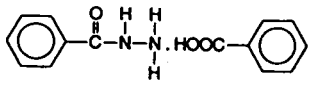
Conical flask method

Corrosion experiments were carried out according to the reported procedure[11] using various ferrous and non-ferrous metals *viz.* mild steel, brass and copper. The specimens of size 2.5×2.0×0.025 cm were used for weight loss measurement studies. Weight loss experiments were carried out in the presence and absence of inhibitors at a fix concentration of 500 ppm, using tight fitting rubber cork 250 mL conical flasks containing 25 mL of water-glycerin mixture to produce 90% relative humidity. The concentration of the inhibitors used for the study was taken according to the volume of the conical flask. The metal specimens were suspended in these bottles by nylon tags and just below these specimens weighed VCIs samples were kept in a glass container which had no contact with the liquid kept inside the conical flask. A battery of conical flasks were kept in an air thermostat set at temperature 40±1 °C and 90% relative humidity during the day and were removed at night to allow condensation of moisture on metal specimen. The experiment was conducted for 20 days. The coupons were placed in inhibited acid bath to remove corrosion products and then weighed. Each experiment was run in duplicate and the average values of weight loss were taken for the study.

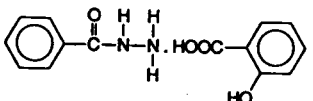
Eschke test

Eschke test was carried out as per reported procedure[12] using various specimens. Polished strips of size 5.0×2.0×0.025cm were wrapped in single layer of inhibitor impregnated Kraft papers and suspended in climatic cabinet maintained at 90% relative humidity. 1 g/ft^2 of various inhibitors were used for the experiment. The temperature cycle was set at 40±1 °C for 12 h and at room temperature for another 12 h for condensation of the moisture. The duration of the test was 20 days. A similar experiment was done with metals covered with untreated Kraft paper (control).

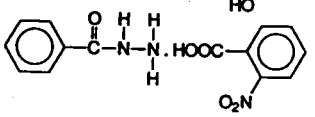
Table 1—Name and molecular structures of the compounds used



Benzoic hydrazide benzoate, (BHB)



Benzoic hydrazide salicylate, (BHS)



Benzoic hydrazide nitrobenzoate, (BHN)

Suphfur dioxide (SO_2) test[12]

Clean and dry specimens of size 5.0×2.0×0.025 cm were placed inside one-liter glass container. Weighed VCI compound was kept inside the container. A small beaker containing 0.04 g of sodium thiosulphate was placed inside the container. 50 mL capacity beaker containing 30 mL aqueous solution of salt (1% NH_4Cl + 1% Na_2SO_4) was placed inside the container. 0.5 mL of 1 N sulphuric acid was directly added to the beaker containing sodium thiosulphate and the glass container was immediately sealed. The glass container was placed in an oven set at 40±1 °C for 16 h and at 10 °C for another 8 h. A similar experiment was done with the one-liter glass container in absence of VCI compound (control).

Salt inoculation test[5]

0.1 g of sodium chloride was placed in 200 mL carbon tetrachloride and the whole solution were stirred by a magnetic stirrer. The metal specimen of size 5.0×2.0×0.025 cm was introduced in the stirred solution for 3-4 s and taken out when approximately 10-12 particles of salt were deposited at random on each side of metal surface. One side of the metal surface was cleaned off the salt particles and the whole metal surface was wrapped in single layer of inhibitor impregnated Kraft papers and suspended in climatic cabinet maintained at 90% relative humidity. 1 g/ft^2 of various inhibitors were used for the experiment. The temperature cycle was set at 40±1 °C for 12 h and at room temperature for another 12 h for condensation of the moisture. The duration of the test was 20 days. A similar experiment was done with metals covered with untreated Kraft paper (control).

Vapour pressure determination

Knudsen method[13] was used to determine the vapour pressure of the inhibitors. Weighed compound was placed in a glass container having an orifice of 1.0 mm diameter. The glass container was then placed in an oven set at 40±1 °C for 20 days. Loss in mass was measured by an electronic balance and the values were put into the formula given as,

$$p = \frac{W}{At} \times \left[\frac{2\pi RT}{M}\right]^{1/2}$$

where, p = vapour pressure of the inhibitor in mm Hg, A = area of the orifice in m^2, t = time of exposure in second, W = weight of evaporated substance in kilogram, T = temperature in Kelvin, M = molecular mass of the compound in kilogram and R = gas constant (8.314 J K^{-1} mol^{-1}). Values of the vapour pressure obtained are given in Table 2.

Results and Discussion

Conical flask method

The values of percentage inhibition efficiency (*% IE*) and corrosion rate (*CR*) obtained by weight loss method in absence and presence of various VCIs for different metals at 40±1 °C are summarized in Table 3. The *% IE* was calculated using the following equation,

$$\% IE = [(CR^{\circ} - CR)/CR^{\circ}] \times 100$$

where CR° and CR are the corrosion rates in the absence and presence of inhibitors, respectively. The corrosion rate was calculated using the following formula[9],

$$CR = \frac{K \times W}{A \times T \times D}$$

where K is a constant (3.45×10^4 mpy, mills per year), W is weight loss in g, A is area of the coupon in cm^2, T is time of exposure in hour and D is density of metal in g/cm^3.

All VCIs have shown good *IE*, which may be attributed to the formation of a physical barrier between metal and corrosive environment by the interaction of metal and inhibitor molecules. However, the difference in their inhibiting action may be due to their different molecular structures.

Eschke test

The values of *% IE* and *CR* obtained by Eschke test are summarized in Table 3. The summary of the visual observations of the test for BHB is represented in Table 4. The graphical representation of CR for all the metals, in the absence (control) and presence of BHB, is shown in Fig. 1.

SO_2 test

The values of *%IE* and *CR* obtained by SO_2 test for 24 h are summarized in Table 3. The result obtained in the presence of SO_2 for BHB is shown in Fig. 2. It is seen that values of CR were reduced considerably in the case of inhibited specimens. The summary of the visual observations of the test for BHB is represented in Table 4. Corrosion of all the metals was reduced considerably in the presence of BHB.

Table 2—Vapour pressures of VCIs

Compounds	Vapour pressure (mmHg)
BHB	0.85×10^{-7}
BHS	2.79×10^{-7}
BHN	2.71×10^{-7}

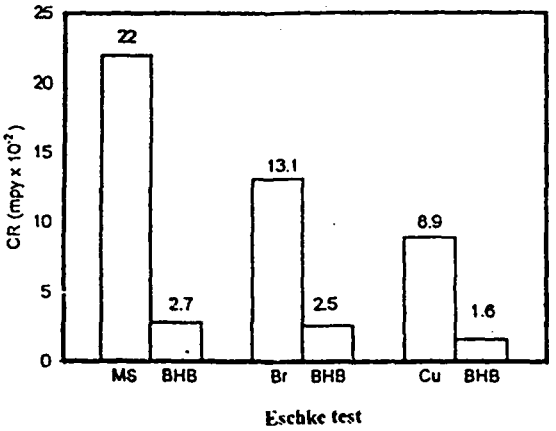


Fig. 1—Results of Eschke test. CR for mild steel, brass and copper in absence and presence of BHB at 40±1°C and 90% relative humidity for 20 days test duration.

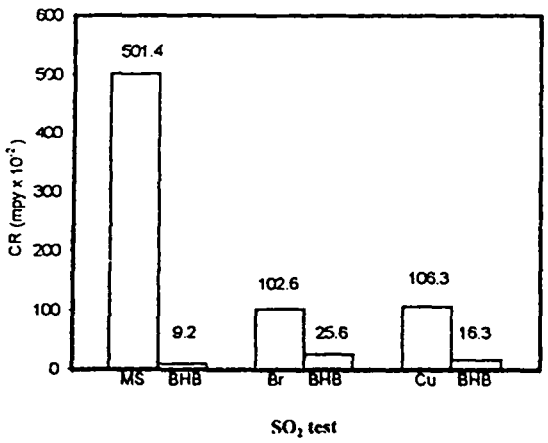


Fig. 2—CR of different metals in absence and presence of BHB in SO_2 environment for 24 h of test duration

Table 3—Weight loss parameters obtained for 500 ppm concentration of VCIs at 40±1 °C and 90% relative humidity for 20 days for various metals

System	Mild steel			Brass			Copper		
	WL (mg)	iE (%)	CR (mpy×10^{-2})	WL (mg)	IE (%)	CR (mpy×10^{-2})	WL (mg)	IE (%)	CR (mpy×10^{-2})
Conical flask method									
Control	34.5	-	320	8.4	-	71	5.7	-	46.0
BHB	1.2	96.6	10.8	0.3	96.4	2.5	0.2	96.5	1.6
BHS	1.3	96.2	12.0	0.5	94.0	4.2	0.5	91.2	4.0
BHN	2.4	93.1	22.0	0.9	89.2	7.6	1.0	82.4	8.1
Eschke test									
Control	4.8	-	22	3.1	-	13.1	2.2	-	8.96
BHB	0.6	87.3	2.7	0.6	80.6	2.5	0.4	82.1	1.6
BHS	1.2	74.7	5.5	0.8	74.1	3.3	0.5	77.2	2.0
BHN	2.6	45.1	12.0	1.3	57.9	5.5	1.0	54.4	4.0
SO_2 test									
Control	5.4	-	501.4	1.2	-	102.6	1.3	-	106.3
BHB	0.2	98.1	9.2	0.3	75.0	25.6	0.2	84.6	16.3
BHS	0.4	92.5	37.1	0.4	66.7	34.1	0.3	76.9	24.5
BHN	1.6	70.3	148.5	0.5	58.3	42.7	0.6	53.8	49.0
Salt inoculation									
Control	54.7	-	207.4	1.9	-	8.0	4.2	-	17.1
BHB	15.4	65.5	71.4	0.7	63.1	2.9	1.5	64.2	6.1
BHS	19.5	56.3	90.4	0.8	57.8	3.3	1.6	61.9	6.5
BHN	26.6	40.4	123.4	1.0	47.2	4.2	2.2	47.6	8.9

Salt inoculation test

The values of *%IE* and *CR* obtained by salt inoculation test are summarized in Table 3. The results obtained when the metal specimens are inoculated with sodium chloride in absence (control) and presence of BHB are shown in Fig. 3. The summary of the visual observations of the test is shown in Table 4. It is also observed visually that in the case of inhibited samples the extent of corrosion around the salt nuclei is restricted and further spreading of the rust was arrested to a considerable extent.

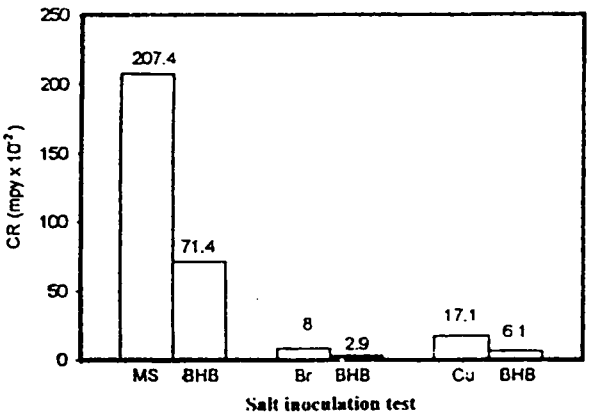


Fig. 3—CR of different metals in absence and presence of BHB in presence of salt at 40±1 °C and 90% relative humidity for 20 days test duration.

Mechanism of corrosion inhibition

Inhibition of metallic corrosion in presence of benzoic hydrazide salts involves vaporization of the inhibitors in a non-dissociated molecular form, followed by hydrolysis of the salts into carboxylate anions ($RCOO^-$) and organic cations ($RCONHNH_3^+$). Anions are adsorbed on the anodic site of the metal and inhibit anodic reaction while organic cations are adsorbed on cathodic side thereby preventing cathodic reaction[14]. The corrosion inhibiting action of the volatile corrosion inhibitors is attributed to the presence of lone pair of electrons present on the N and O atoms of the inhibitor molecules, which facilitate adsorption of these inhibitors onto the metal surface. The presence of extensively delocalised

Table 4—Visual observations of the metal surface in the presence and absence of BHB from various test methods

System	Visual observation		
	Eschke test	SO_2 test	Salt inoculation test
Mild steel (Control)	Moderate to heavy rusting.	Severely rusted all-over the surface.	Whole surface covered with patches of brownish-red spots.
BHB	No rusting, bright surface.	No rusting, bright surface.	Rusting restricted to nuclei, rest of the surface bright and unattacked.
Brass *(Control)*	Moderate to heavy tarnishing.	Moderate to heavy tarnishing.	Rusting around nuclei, heavy tarnishing.
BHB	Slight tarnishing.	Slight tarnishing.	Slight rusting around nuclei.
Copper (Control)	Moderate to heavy tarnishing.	Heavy tarnishing.	Rusting around nuclei, heavy tarnishing
BHB	Slight tarnishing.	Slight tarnishing.	Slight rusting around nuclei, slight tarnishing.

π-electrons on benzene ring further facilitates adsorption process. In the present investigation, benzoate salt exhibited highest *IE* (i.e., >96%) for all the metals studied. Lesser *IE* of salicylate salt may be attributed to the orientation of the substituent group (–OH) at ortho position, which prevents flat orientation on the metal surface causing less adsorption thereby less inhibition. The lesser *IE* of nitrobenzoate salt may be attributed to the –I effect of $-NO_2$ group which reduces its adsorption at the active sites of the metal surface.

Conclusion

All the tested organic inhibitors showed good inhibition efficiency (*IE*) for mild steel, brass and copper. The benzoate salt exhibited highest *IE* for all the metals. The order of the *IE* for various inhibitors for all the metals follows the order BHB > BHS > BHN.

Acknowledgement

Two of the authors (DJ) and (VB) thankfully acknowledge CSIR, New Delhi, India for the award of Research Associateship and Senior Research Fellowship, respectively.

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CORROSION2003

INHIBITION OF METALLIC CORROSION BY SOME 2-CINNAMYL IMIDAZOLINE SALTS UNDER VAPOR PHASE CONDITIONS

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ABSTRACT

Four organic volatile corrosion inhibitors (VCIs) were synthesized using 2-cinnamyl imidazoline with various acids such as salicylic acid, maleic acid, nitrobenzoic acid and phthalic acid and evaluated as corrosion inhibitors of mild steel, brass and copper by weight loss method. Eschke test method, sodium chloride inoculation test method and sulfur dioxide (SO_2) test method were also carried out to investigate the corrosion inhibiting effect of the compounds. All the investigated VCIs exhibited good inhibition efficiency (IE) for all the metals. Phthalate salt showed best result among all studied compounds for all the metals.

Keywords: Eschke test, ferrous and non-ferrous metals, imidazoline salts, salt inoculation test, sulfur dioxide test, volatile corrosion inhibitor

INTRODUCTION

The volatile corrosion inhibitors are used to protect metallic articles and equipments in enclosed atmosphere [1]. The choice of a chemical compound as a vapor phase corrosion inhibitor (VCI) depends on its vapor pressure and efficiency to prevent corrosion by forming a protective film. There are numerous investigations on corrosion inhibition studies utilizing aliphatic amines, alicyclic amines and their salts as VCIs for various industrial metals and alloys [2-4]. Fatty acid amines are more effective than cyclic amines and aromatic amines [4]. 1, 3-Dinitrobenzene with β-Naphthol was examined as VCI in SO_2 and chloride atmosphere by Rajagopalan, et al., [5]. Subramanian, et al., [6] studied corrosion inhibitive performance of cyclohexylamine (CHA) salts and dicyclohexylamine (DCHA) salts on copper, mild steel and zinc in SO_2 environment. DCHA exhibited 70.86, 85.15 and 91.81% inhibition efficiency (IE) in mild steel, copper and zinc respectively. Subramanian, et al.[7] has recently studied the corrosion inhibition behavior of morpholine and its three salts such as morpholine carbonate, borate and phosphate

salts. Of these, morpholine and its carbonate salt exhibited 90% and 85% IE, respectively, while the other salts gave less than 40% IE.

Continuing our recent work [8-9] on vapor phase corrosion inhibitors, we report here the inhibiting properties of four organic vapor phase inhibitors (VCIs) namely, 2-cinnamyl imidazoline salicylate (CIS), 2-cinnamyl imidazoline maleate (CIM), 2-cinnamyl imidazoline nitrobenzoate (CIN) and 2-cinnamyl imidazoline phthalate (CIP) on mild steel, brass and copper.

EXPERIMENTAL

Synthesis of the organic compounds

2-cinnamyl imidazoline was synthesized according to the procedure reported in the literature[10] and the salts were prepared by dissolving equimolar fatty acid imidazoline and organic acids in ethanol. The reaction mixture was stirred for 1.0 hour at 40 ^{0}C. The precipitated compounds were filtered and crystallized from ethanol. M.P^{o}C (CIS=62, CIM=95, CIN=115, CIP=98). All compounds were purified by crystallization and their purity was confirmed by thin layer chromatography. Name and molecular structure of the compounds are presented in Table1.

Weight loss measurements

Corrosion experiments were carried out according to the procedure reported in the literature[11] using various ferrous and non-ferrous metals viz. mild steel, brass and copper. The specimens of size 2.5 cm x 2.0 cm x 0.025 cm (0.984 in. x 0.787 in. x 0.0098 in.) were used for weight loss measurement studies. Weight loss experiments were carried out in the presence and absence of inhibitors at a fix concentration of 500 ppm, using tight fitting rubber cork 250mL conical flasks containing 25mL of water-glycerin mixture to produce 90% relative humidity. The concentration of the inhibitors used for the study was taken according to the volume of the conical flask. The metal specimen were suspended in these bottles by nylon tags and just below these specimens weighed VCIs samples were kept in a glass container as not to be in contact with the liquid kept inside the conical flask. A battery of conical flasks were kept in an air thermostat set at temperature 40±1^{0}C and 90 % relative humidity during the day and were removed at night to allow condensation of moisture on metal specimen. The experiment was conducted for 20 days. The coupons were placed in inhibited acid bath to remove corrosion products then weighed.

Eschke Test

Eschke test was carried out as per procedure reported in the literature[12] using various metals strips of size 5.0 cm x 2.0 cm x 0.025cm (1.968 in. x 0.787 in. x 0.0098 in.) were wrapped in single layer of inhibitor impregnated Kraft papers and suspended in climatic cabinet maintained at 90% relative humidity. 1 gm/ft.^{2} of various inhibitors were used for the experiment. The temperature cycle was set at 40±1^{0}C for 12 hours and at room temperature for another 12 hours for condensation of the moisture. The duration of the test was 14 days. A similar experiment was done with metals covered with untreated Kraft paper (control).

Sulfur dioxide (SO_2) test[13]

Clean and dry metal specimens 5.0 cm x 2.0 cm x 0.25cm (1.968 in. x 0.787 in. x 0.098 in.) were placed inside one-liter glass container. Weighed VCI compound was kept inside the container. A small beaker containing 0.04 g of sodium thiosulphate was placed inside the container. 50-ml capacity beaker containing 30-ml. aqueous solution of salt (1% NH_4Cl + 1% Na_2SO_4) was placed inside the container. 0.5 ml of 1N sulfuric acid was directly added to the beaker containing sodium thiosulphate and the glass container was immediately sealed. The glass container was placed in an oven set at 40±1^{0}C for the duration of 16 hours and at 10 ^{0} C for another 8 hours. A similar experiment was done with the one-liter glass container in absence of VCI compound (control).

Salt inoculation test [6]

0.1 g of sodium chloride was placed in 200 ml carbon tetrachloride and the whole solution was stirred by a magnetic stirrer. The metal specimen 5.0 cm x 2.0 cm x 0.25cm (1.968 in. x 0.787 in. x 0.098 in.) was introduced in the stirred solution for 3-4 seconds and taken out when approximately 10-12 particles of salt were deposited at random on each side of metal surface. One side of the metal surface was cleaned off the salt particles and the whole metal surface was wrapped in single layer of inhibitor impregnated Kraft papers and suspended in climatic cabinet maintained at 90% relative humidity. 1 gm/ft.^{2} of various inhibitors were used for the experiment. The temperature cycle was set at 40±1^{0}C for 12 hours and at room temperature for another 12 hours for condensation of the moisture. The duration of the test was 14 days. A similar experiment was done with metals covered with untreated Kraft paper (control).

Vapor pressure determination

A standard Knudsen method [13] was used to determine the vapor pressure of the inhibitors. Weighed compound was placed in a glass container having an orifice of 1.0 mm diameter. The glass container was then placed in an oven set at 40±1^{0}C for 20 days. Loss in mass was measured by an electronic balance and the values were put into the formula given below:

$$p = \frac{W}{At} \times \left(\frac{2\pi R T}{M}\right)^{1/2}$$

where, p = vapor pressure of the inhibitor in mm Hg, A = area of the orifice in m^2, t = time of exposure in second, W = weight of evaporated substance in kilogram, T = temperature in Kelvin , M = molecular mass of the compound in kilogram and R = gas constant (8.314 J K^{-1} mol^{-1}). Values of the vapor pressure obtained are given in Table 2.

RESULTS AND DISCUSSION

Weight loss measurement

The values of percentage inhibition efficiency (%IE) and corrosion rate (CR) obtained by weight loss methods at 500 ppm concentration of VCIs for different metals at 40±1^{0}C are summarized in Table 3. The %IE was calculated using the following equation:

$$\%IE = [(CR^0 - CR)/ CR^0] \times 100$$

where CR^0 and CR are the corrosion rate in the absence and presence of inhibitors, respectively. The corrosion rate was calculated using the following formula:

$$CR = \frac{K \times W}{A \times T \times D}$$

where K is a constant (8.76 x 10^4 for mmpy, millimeters per year), W is weight loss in g , A is area of the coupon in cm^2, T is time of exposure in hour and D is density of metal in gm/cm^3.

All VCIs have shown good IE, which may be attributed to the formation of a physical barrier between metal and corrosive environment by the interaction of metal and inhibitor molecules. The corrosion inhibiting action of the volatile corrosion inhibitors is attributed to the presence of lone pair of electrons present on the N atoms of the inhibitor molecules, which facilitate adsorption of these

inhibitors onto the metal surface. Phthalate salt exhibited highest IE for all the metals. It gave 95.7%, 86.08% and 93.1% for mild steel, brass and copper respectively.

Eschke Test

The summary of the visual observations of the test is represented in Table 4. It is seen that a large spread of results were obtained. The graphical representation of all the metals with respect to CR in the absence (control) and presence of CIP is shown in Fig. 1.

SO_2 Test

The result obtained in the presence of sulfur dioxide is shown in Fig. 2. It is seen that values of CR was reduced considerably in the inhibited metal specimens. The summary of the visual observations of the test is represented in Table 4. Corrosion of all the metals was reduced considerably in the presence of CIP.

Salt inoculation test

The result obtained when the metals are inoculated with sodium chloride in absence (control) and presence of CIP is shown in Fig. 3. The summary of the visual observations of the test is shown in Table 4. It is also observed visually that in the case of inhibited samples the extent of corrosion around the salt nuclei is restricted and further spreading of the rust was arrested to a considerable extent.

MECHANISM OF CORROSION INHIBITION

Inhibition of metallic corrosion in presence of 2-cinnamyl imidazoline salts involves vaporization of the inhibitors in a non-dissociated molecular form, followed by hydrolysis of the salts into carboxylate anions ($RCOO^-$) and organic cations ($RCONHNH_3^+$). Anions are adsorbed on the anodic site of the metal and inhibit anodic reaction while organic cations are adsorbed on cathodic side thereby preventing cathodic reaction [14]. Corrosion inhibiting action of the imidazoline is attributed to the presence of π-electrons and lone pair of electrons present on N atoms of the imidazoline molecule, which facilitate adsorption of inhibitor molecules onto the metal surface.

Acknowledgement

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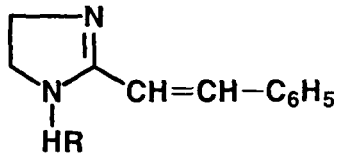
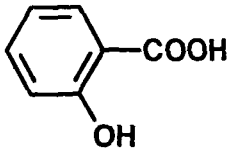
TABLE-1
MOLECULAR STRUCTURES OF VCIs

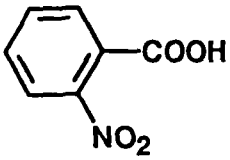


1. R = 

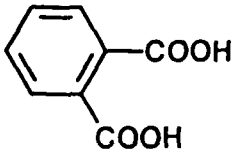
2-cinnamyl imidazoline salicylate (CIS)

2. R = $HO_2CCH = CHCO_2H$

2-cinnamyl imidazoline maleate (CIM)

3. R = 

2-cinnamyl imidazoline nitrobenzoate (CIN)

4. R = 

2-cinnamyl imidazoline phthalate (CIP)

'TABLE-2

VAPOR PRESSURE OF VCIs

S. No.	Vapor Pressure (mmHg)	Compounds
1.	84×10^{-7}	CIS
2.	22.2×10^{-5}	CIM
3.	10.2×10^{-6}	CIN
4.	10.5×10^{-6}	CIP

TABLE-3

WEIGHT LOSS PARAMETERS OBTAINED FOR 500 PPM CONCENTRATION OF VCIs AT 40±1 ^{0}C AND 90% RELATIVE HUMIDITY FOR 20 DAYS FOR VARIOUS METALS.

System	Weight loss (mg)	IE (%)	Corrosion rate (mmpy $x10^{-2}$)
Mild Steel	34.5	-	8.00
CIS	2.8	92.00	0.65
CIM	2.3	93.37	0.53
CIN	1.9	94.50	0.44
CIP	1.5	95.75	0.35
Brass	8.4	-	1.79
CIS	2.4	71.50	0.51
CIM	1.7	79.88	0.36
CIN	1.5	82.68	0.32
CIP	1.2	86.03	0.25
Copper	5.7	-	1.16
CIS	1.3	77.58	0.26
CIM	0.9	84.48	0.18
CIN	0.6	89.65	0.12
CIP	0.4	93.10	0.08

TABLE-4

VISUAL OBSERVATIONS OF THE METAL SURFACE IN THE PRESENCE AND ABSENCE OF CIP FROM VARIOUS METHODS.

System	Visual Observations		
	Eschke Test	SO_2 Test	Salt Inoculation Test
Mild Steel (Control)	Moderate to heavy rusting.	Severely rusted all-over the surface	Whole surface covered with patches of brownish-red spots.
CIP	2-3 rusted spot.	No rusting; Bright Surface.	Rusting restricted to nuclei, rest of the surface bright and unattacked.
Brass (Control)	Moderate to heavy tarnishing.	Moderate to heavy Tarnishing.	Rusting around nuclei.
CIP	Slight tarnishing.	Slight tarnishing.	Slight rusting around nuclei.
Copper (Control)	*Moderate to heavy tarnishing.*	*Heavy tarnishing.*	*Rusting around nuclei.*
CIP	Slight tarnishing.	Slight tarnishing.	Slight rusting around nuclei.

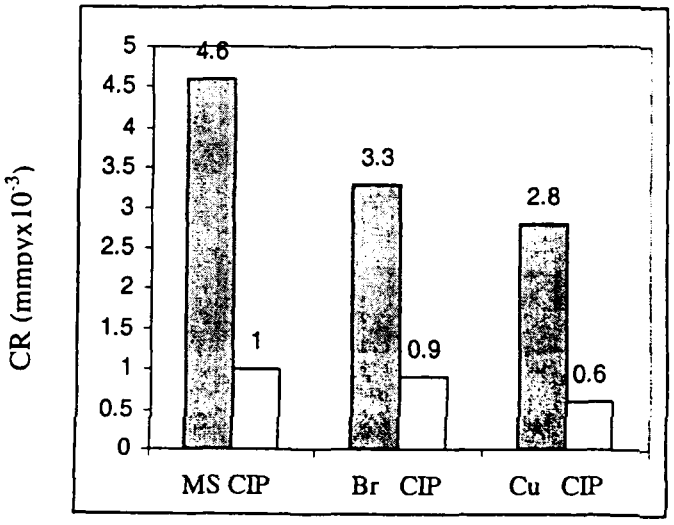


FIG. 1. Results of Eschke Test. CR for Mild steel, Brass and Copper in absence and presence of for OIP at 40 ± 1 ^{0}C and 90% relative humidity for 14 days test duration

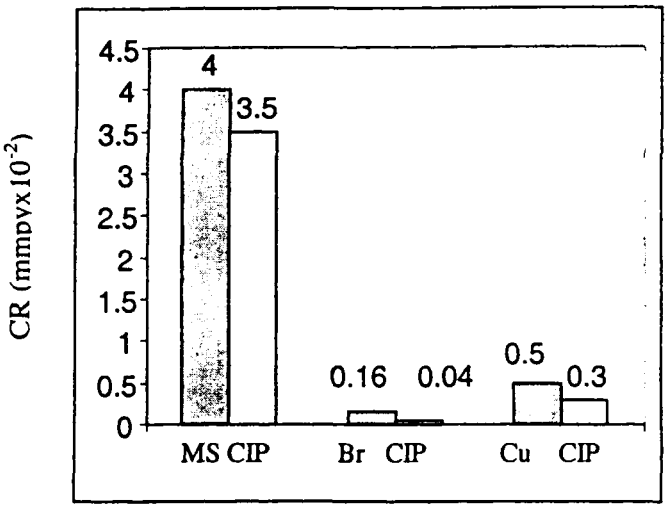


FIG. 2. CR of different metals in absence and presence of CIP in SO_2 environment for 24 hours of test duration.

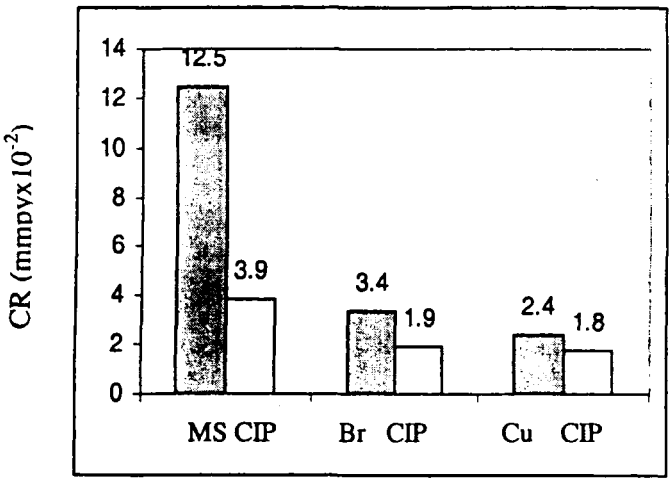


FIG. 3. CR of different metals in absence and presence of CIP in presence of salt at $40 \pm 1\ ^0C$ and 90% relative humidity for 14 days test duration.